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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
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PART II.

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### General and Physical Chemistry.

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**A New Method of Expressing the Formulæ of Line Spectra**  
ALFRED LARTIGUE (*Compt. rend.*, 1919, 169, 914—915).—In place of the general formula  $10^8/\lambda = N_0(1/p^2 - 1/q^2)$  waves per cm., the author proposes to use the formula  $\lambda_m = (4 \times 10^8/N_0)(p/2)^3[2/p + m - 1/(m + 2p)]$  Angströms, where  $m = q - p$ . W. G.

**Luminous Phenomena Observed in the Neighbourhood of a Plate of Graphite raised to a High Temperature by means of an Electric Current.** G. A. HEMSALECH (*Compt. rend.*, 1919, 169, 915—918).—A sheet of graphite 0.95 mm. thick had its upper surface covered with a thin layer of carborundum powder, and an electric current was passed through it. As the temperature of the plate increased, when it became incandescent, yellow vapours appeared above the plate and were carried upwards by the air convection currents. When the temperature of the plate reached 2500—2700°, the space bounded by the plate and the air convection currents became filled with a luminous vapour which gave a spectrum composed of rays and bands, whilst the yellow vapours became blue and also luminous, and gave a continuous spectrum. When the temperature of the plate reached 3000°, a red fringe appeared on its lower surface and in contact with it, and was formed by the passage of an electric current through the conducting vapours. Its position could be controlled

by means of the magnetic field from a powerful electro-magnet. This red fringe is of electrical origin, and is probably due to a current of electrons, which decompose the molecules and create centres of emission differing from those of the luminous vapour.

W. G.

**The Spectra Emitted by the Red Fringe and the Luminous Vapour in the Neighbourhood of an Incandescent Plate of Graphite.**

G. A. HEMSALECH (*Compt. rend.*, 1919, 169, 1034—1036).—It has previously been shown that the luminous vapour and red fringe obtained when a plate of graphite is raised by an electric current to high temperatures emit discontinuous spectra (preceding abstract). These spectra have now been examined in detail, and the rays which have been detected are given and the influence of a magnetic field on the centres of emission examined. The spectra of bands and rays, obtained under the experimental conditions, owe their origin to two different types of centres of emission: (1) Those created by the action of heat on the carbides of the metals, the spectrum of which is regulated by the temperature of the graphite plate. The centres of emission are not sensibly influenced by a magnetic field. (2) Those produced by the thermo-electric current, the spectrum of which is regulated both thermally and electrically. The centres of emission are, in this case, very sensitive to magnetic forces.

W. G.

**Reduction Spectra, and in particular that of Magnesium and its Compounds.**

J. MEUNIER (*Bull. Soc. Chim.*, 1919, [iv], 25, 562—565).—Using the method previously described, by reduction in a hydrogen flame (compare A., 1919, ii, 132) the author finds in the ultraviolet region the band composed of the rays  $\lambda = 3810, 3829, 3833, 3838, 3851, 3858, 3861$ , and another band consisting of the rays  $\lambda = 3885, 3912, 3940, 3960, 3980$ . Nine other rays between  $\lambda = 3700$  and  $3780$  have been noticed and their wavelengths approximately determined. Of the salts of magnesium, the chloride, oxychloride, sulphate, nitrate, oxide, and carbonate gave the above spectrum. The pyrophosphate is not, apparently, reduced under these conditions and does not give the above spectrum, phenomena of incandescence, corresponding with the continuous spectrum, being produced.

In some cases, the  $\gamma$ -ray in the neighbourhood of  $\lambda = 5003$ , and the broad magnesium ray,  $\lambda = 4702$ , are obtained.

W. G.

**The X-ray Spectrum of Tungsten.**

M. DE BROGLIE (*Compt. rend.*, 1919, 169, 962—965).—Certain observations, as a result of a long series of experiments, are made on the results of Overn and of Siegbahn (A., 1919, ii, 488) on the spectrum of tungsten. Some of the lines mentioned by Overn the author has not found, whilst on the other hand he has observed certain rays not mentioned by Overn.

For the purpose of obtaining weak bands, the author advocates

the use of a metal shutter pierced with a slit and travelling in front of the sensitive plate with a velocity such that, during the rotation of the crystal, the reflected ray passes continuously through the slit.

W. G.

**Relative Brightness of Dark Radiation at the Melting Points of Gold and Palladium.**

FR. HOFFMANN and W. MEISSNER (*Ann. Physik*, 1919, [iv], **60**, 201—232).—The relative brightness of the dark radiation at the melting points of gold and palladium has been measured by two different methods: first, by use of an improved hollow radiator constructed on the Lummer-Kurlbaum principle, whereby the melting point was determined inside the radiator by the wire method; secondly, by use of a hollow radiator which was immersed in the molten metal. The measurements of brightness were made with a König-Martens spectrophotometer. The relative brightness at the melting points of gold and palladium is expressed by 81.5 at the wave-length of  $0.6563\mu$ . The palladium used had the same melting point as that used by Day and Sosman in the gas thermometric measurements. Palladium prepared by repeated precipitation of the ammonium double chloride by means of mercury cyanide gave a very constant melting point, and would serve excellently as a fixed point for temperature determinations. Using  $c=14,300$  as the radiation constant and  $1063^\circ$  as the melting point of gold, it is found that  $1557^\circ$  is the melting point of palladium. This value is about  $8^\circ$  higher than Day and Sosman's figure,  $1549.2^\circ$ .

J. F. S.

**The Ozonogenic Power of the Solar Radiation at the Altitude of the Observatory of Mont Blanc.**

RAOUL BAYEUX (*Compt. rend.*, 1919, **169**, 957—959).—At an altitude of 4360 metres, the solar radiation does not cause the polymerisation of oxygen to ozone.

W. G.

**The Absorption of Light by Gases.**

G. RIBAUD (*Ann. Physique*, 1919, [ix], **12**, 107—226).—A study of the continuous absorption by bromine vapour in the ultraviolet portion of the spectrum, the conditions being varied as much as possible, the temperature range rising to  $620^\circ$ . The observed experimental curves show notable systematic divergences from the theoretical curves based on the electromagnetic theory of absorption, the weakening (*amortissement*), in particular, calculated for the different regions of the curve, not having the same value. The kinetic theory does not apply to the broad, continuous regions of absorption, and the mechanism of the absorption must be sought in the molecule itself. The author is of the opinion that the weakening (*amortissement*) can be explained by the disturbances of the electron in the interior of the molecule. This conception permits of an explanation of the fact that the breadth of the bands goes on increasing from the ultraviolet to the infra-red.

It is shown that Königsberger's law, that the breadth of the



band is proportional to the square root of the temperature, must be rejected.

In the last part of the paper it is shown that the absorption by the rays of bromine vapour is in close accord with a kinetic theory of absorption, and, in this case, the mobile corpuscle containing the electron is, in all probability, the molecule itself. The magneto-optical properties of the vapours of bromine and iodine in the neighbourhood of the absorption rays have been studied, and it is shown that the rotatory phenomenon observed in the neighbourhood of these rays in iodine vapour is due to a very weak Zeeman effect. The smallness of this effect agrees moderately well with the small values observed for the ratio  $e/m$  in the absorption study.

W. G.

**Chemical Actions of Light.** E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 432—436).—When subjected to prolonged exposure to light, ethyl alcohol does not undergo oxidation, but in presence of oxalic acid it is slowly oxidised in the light, yielding carbon dioxide and formic and acetic acids. Under similar conditions, glycerol (8 grams) gives carbon dioxide, together with other oxidation products equivalent, in their reducing action on Fehling's solution, to 0.351 gram of dextrose. When exposed to light in an atmosphere of oxygen and in presence of water, thiophen yields carbon dioxide and formic, oxalic, and sulphuric acids. Similarly, a benzene solution containing benzophenone and dibenzyl gives rise to benzophenonepinacone and *triphenylbenzyl-ethanol* [ $\alpha\alpha\beta\gamma$ -tetraphenylpropyl alcohol],  $\text{OH}\cdot\text{CPh}_2\cdot\text{CHPh}\cdot\text{CH}_2\text{Ph}$ , which crystallises in long needles, m. p.  $165^\circ$ . In the light, benzoquinone and toluene react to form quinol, quinhydrone, and a small proportion of benzaldehyde. Acetone and *isoamyl* alcohol also react under these conditions, the products identified being (1) *isopropyl* alcohol; (2) *dimethylisobutylene glycol* [ $\beta\beta$ -dimethylhexane- $\beta\gamma$ -diol],  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{OH}$ , b. p.  $136$ — $137^\circ/81$  mm.; (3) *disobutylene glycol* [ $\beta\gamma$ -dimethyloctane- $\delta\epsilon$ -diol],

$\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CHMe}_2$ ,  
m. p.  $92^\circ$ , which is formed in accordance with the equations:  
 $\text{CH}_3\cdot\text{COMe} + \text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH} =$   
 $\text{CHMe}_2\cdot\text{OH} + \text{CHMe}_2\cdot\text{CH}_2\cdot\text{CHO};$

the latter  
 $+ \text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH} =$   
 $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CHMe}_2$

(4) resinous products not identified.

T. H. P.

**Photochemical Studies. V. Triboluminescence.** JOSE PLOTNIKOV (*Prometheus*, 1919, **30**, 235—236; from *Chem. Zentr.*, 1919, iv, 462—463).—An apparatus is described with which triboluminescence can be excited under constant, comparable conditions. The triboluminiscope consists of a marble cylinder on which a thick glass plate is pressed, the pressure being regulated by two screws. The substance under investigation is placed between the

plate and the cylinder, and, on rotation of the latter, becomes ground at the point of contact. If the substance is triboluminescent, an illuminated band appears which shines continuously if the rotation is uniform. A special type of camera intended for use in photographing the band is also described. If the substances under investigation are hard enough to abrade the apparatus, the latter is formed from an agate cylinder and a quartz plate. For purposes of demonstration, the use of salophen, which gives a pale green triboluminescence, is recommended.

H. W.

#### Relationship between the Range and the Life of $\alpha$ -Rays.

F. KIRCHOF (*Zeitsch. physikal. Chem.*, 1919, **93**, 619—622).—It is shown that the range of the  $\alpha$ -ray emitted by all radioactive elements is shorter the greater the life of the atom producing it. On plotting the range against the half-life, three similar curves are obtained, one for each radioactive family. On plotting the logarithms of the range against the logarithms of the half-life, curves are obtained which indicate that with a range, zero, the life is not infinitely large, but has a finite value about  $10^{15}$ — $10^{18}$  years. Applying this result to Ra-G, the author concludes that it is disintegrating at the above-named rate, but that its  $\alpha$ -ray has no penetrating power. It is also deduced that the  $\alpha$ -rays from isotopes have not the same range, but values corresponding with their own family.

J. F. S.

#### The Radioactivity of Uranium.

CHARLES STAHLING (*Compt. rend.*, 1919, **169**, 1036—1039).—The oxides of uranium studied were obtained from different sources after careful purification and subsequent calcination either of uranyl nitrate or ammonium nitrate. The activities of such oxides were followed over the period from January 13th, 1913, to July 18th, 1914, and a further series of measurements were made in November, 1919. All the oxides studied showed a lowering in penetrating activity varying from 1 to 30.7%, and the curves indicate that half the lowering took place in 6.2 months. The lowering was greatest in the case of the green oxides and least with the black oxides. In the case of a blackish-green oxide, which showed a lowering from 5.95 to 4.64; when this oxide was dissolved in nitric acid and the nitrate again calcined, giving the black oxide, the activity rose again to 5.90. If then this oxide was converted into the green oxide by passage through ammonium uranate, it retained its high restored activity. Renewing the surfaces of the disks did not modify the activities observed.

W. G.

#### Dependence of the Di-electric Constant of Gases on Temperature.

HANS RIEGER (*Ann. Physik*, 1919, [iv], **59**, 753—760).—The dielectric constants for air, hydrogen, methane, carbon dioxide, and carbon monoxide have been measured at low temperatures, and a series of pressures (200—760 mm.) by Mandelstam's dynamometer method (*ibid.*, 1910, **33**, 490). The

results are calculated to 760 mm. pressure in each case by the formula  $(\epsilon_1 - 1)/(\epsilon_2 - 1) = \rho_1/\rho_2$ , and the values for  $\epsilon - 1$  found as follows: air ( $-185.5^\circ$ ), 0.001902; hydrogen ( $-191^\circ$ ), 0.000928; methane ( $-154^\circ$ ), 0.00216; carbon dioxide ( $-73^\circ$ ), 0.001392; carbon monoxide ( $-189^\circ$ ), 0.002633. The values are compared in all cases with those at ordinary temperatures ( $16-18.5^\circ$ ) and 760 mm. pressure.

J. F. S.

### The Theory of Electrolytic Ions. XI. The Limiting Values of Molecular Conductivity and their Determination.

RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1919, 108, 81—110).—

The limiting value,  $\mu_\infty$ , of electrical conductivity can be calculated from the so-called Ostwald-Bredig rule,  $\mu_\infty = \mu + \Delta$ , where  $\Delta$  varies with the dilution at which  $\mu$  is observed. The values of  $\Delta$  were determined empirically for the sodium salts of different acids and the chlorides of different bases by Bredig, and are given in his tables for dilutions from 32 to 1024. Two formulæ were given by Kohlrausch for calculating  $\mu_\infty$ , (1) for very high dilutions,  $\mu_\infty - \mu = a[S_0]^{\frac{1}{2}}$ , and (2) for less high dilutions,  $\mu_\infty - \mu = b[S_0]^{\frac{1}{2}}$ , in which  $[S_0]$  is the concentration of the salt and  $a$  and  $b$  are constants. A statistical study of the data available for a very large number of organic cations of the ammonium type has now been made with the object of determining which of these formulæ gives the most reliable values of  $\mu_\infty$ . Both graphic and algebraic methods were used in applying the two Kohlrausch formulæ, and the values found for the constants  $a$  and  $b$  were practically the same by both methods. It was found that  $a$  and  $b$  are undoubtedly "universal" constants, since the deviations from the mean value show no relation to the constitution of the ions. The mean values are  $a$ , 91.54;  $b$ , 58.2. The values of  $\Delta$  in the Ostwald-Bredig formula can be calculated from either of the above equations when the constants are known. When compared with the values given by Bredig, those obtained from the first equation show the best agreement, but this is no proof of their superiority. The two equations give slightly different values for  $\mu_\infty$ , but it is impossible to decide which is the more accurate. From the study of the data for a number of inorganic salts, it was similarly impossible to decide between the two formulæ.

E. H. R.

### The Theory of Electrolytic Ions. XII. The Limiting Values of Molecular Conductivity and Kohlrausch's Extrapolation Law.

RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1919, 108, 191—210. Compare preceding abstract).—For the determination of  $\Delta$  from the relation  $\mu_\infty = \mu + \Delta$ , values of  $\Delta$  are given in Bredig's tables for dilutions from 32 to 1024, these values being applicable to all sodium salts of univalent anions and all chlorides of univalent cations. Bredig's values for  $\Delta$  were arrived at empirically, but they can be calculated from Kohlrausch's equation,  $\mu_\infty - \mu = a[S_0]^{\frac{1}{2}}$ . This calculation has been made for a large number of inorganic salts, the conductivities of which have been accurately

determined, and when the values of  $\Delta$  so obtained are compared with those given by Bredig, considerable disagreement is found. It is shown on theoretical grounds that Bredig's rule is unsound; it gives only a rough approximation to the true value of  $\mu_{\infty}$ . A critical examination of Kohlrausch's conductivity measurements of inorganic salts shows that the formula  $\mu_{\infty} - \mu = a[S_0]^{\frac{1}{2}}$  expresses the results with a high degree of precision for dilutions from 10,000 to 100, whilst from 100 to 10 the formula  $\mu_{\infty} - \mu = b[S_0]^{\frac{1}{3}}$  is better. A more general expression is  $\mu_{\infty} - \mu = A[S_0]^n$ , where  $A$  and  $n$  are functions of the dilution. Whilst in the series of salts of univalent organic cations, the constants  $a$  and  $b$  of the above extrapolation formulæ retain the same value throughout the series (see preceding abstract), in the case of the inorganic salts of univalent cations the values of these constants increase with the atomic weight of the cation in a series such as that from lithium nitrate to caesium nitrate.

E. H. R.

**Conductivity. V. Measurement of the Conductivity of Solutions.** H. I. SCHLESINGER and F. H. READ (*J. Amer. Chem. Soc.*, 1919, **41**, 1727—1732).—It is shown that although the minima obtained in the measurement of the electrical resistance of solutions may be perfectly sharp, nevertheless the results may be incorrect. This difficulty can be overcome by placing the telephone across the ends of the bridge wire and using an air condenser in parallel with the smaller capacity. It is also shown that the "cell-constant" ought to be determined from solutions which cover the whole range of resistance eventually to be measured.

J. F. S.

**Equilibria Across a Copper Ferrocyanide and an Amyl Alcohol Membrane.** FREDERICK GEORGE DONNAN and WILLIAM EDWARD GARNER (*T.*, 1919, **115**, 1313—1328).

**The Action Exerted by Antagonistic Electrolytes on the Electrical Resistance and Permeability of Emulsion Membranes.** G. H. A. CLOWES (*Proc. Soc. Expt. Biol. Med.*, 1918, **15**, 108—111).—The author brings forward various experimental data derived from electrical conductivity and permeability experiments with artificial emulsion membranes in support of his contention that variations in the permeability of the protoplasmic membrane are attributable to the action of electrolytes and metabolic products on delicately balanced interfacial soap films and emulsion systems and that proteins play no part in the valve-like mechanism controlling permeability other than to afford a supporting filamentous or mesh-like structure. In support of this it is further pointed out that when blood plasma is clotted by the addition of calcium chloride no considerable change in electrical resistance is noted, whilst in the transformation of an emulsion of oil in water into one of water in oil by shaking with calcium chloride the resistance suddenly rises to an enormous extent at the critical point at which oil becomes the continuous or external phase. This all fits in with the well known fact that alkalis, salts of sodium, potassium, etc.,

promote the permeability of tissues whilst salts of calcium, magnesium, and other bi- and ter-valent cations exert the reverse effect, also with the high potassium content and low calcium content of rapidly growing tumours and the reverse relation in slow-growing or stationary tumours.

CHEMICAL ABSTRACTS.

**Phenomenon after Anodic Polarisation. I.** A. SMITS, G. L. C. LA BASTIDE, and J. A. VAN DEN ANDEL (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 82—88).—When the metals iron, nickel, and chromium are anodically polarised in solutions of their salts, using a current density of a definite value, and the potential measured after the polarising current has been broken, it is found that the potential passes through a minimum and then rises to the value before polarisation. Similar experiments with copper and silver did not produce the same effect, so that it appears this phenomenon is only shown in solutions where ions of two stages of oxidation exist or may exist. To test this point the experiment was repeated with iron, using a solution of ferrous chloride, which had been freshly boiled with iron powder, an atmosphere of hydrogen being used. The results show that the minimum potential is no longer observed, and that qualitatively, at least, iron behaves like copper and silver.

J. F. S.

**Potentials of the Zinc and Cadmium Electrodes.** W. GRENVILLE HORSCH (*J. Amer. Chem. Soc.*, 1919, **41**, 1787—1800).—The *E.M.F.* of the following cells has been determined at 25°:  $\text{Zn}|\text{ZnCl}_2|\text{AgCl}|\text{Ag}$ ;  $\text{Cd}(\text{amalgam})|\text{CdCl}_2|\text{AgCl}|\text{Ag}$ ;  $\text{Cd}(\text{amalgam})|\text{CdCl}_2|\text{Cd}$ ; and  $\text{H}_2|\text{HCl}(0.01N)|\text{AgCl}|\text{Ag}$ . In the first cell the concentrations of zinc chloride solution varied from 0.0003*M* to 0.01*M*; in the second the concentration of cadmium chloride varied from 0.0001*M* to 6.61*M* (saturated). The normal electrode potentials of zinc and cadmium were found to be  $0.758 \pm 0.002$  volt and  $0.3992 \pm 0.0010$  volt respectively, the normal hydrogen electrode being taken as zero. The free energy of dilution of zinc chloride and cadmium chloride solution was calculated, and the following values obtained:

$c_1$ .	$c_2$ .	$F(\text{CdCl}_2)$ .	$F(\text{ZnCl}_2)$ .
0.1 <i>M</i>	0.01 <i>M</i>	1306 cal.	—
0.01 <i>M</i>	0.001 <i>M</i>	1615 cal.	1719 cal.
0.005 <i>M</i>	0.0005 <i>M</i>	1705 cal.	1858 cal.

J. F. S.

**The Effect of Amalgamation on the Single Potential of Aluminium.** LOUIS KAHLENBERG and JOHN A. MONTGOMERY (*Trans. Amer. Electrochem. Soc.*, **36**, 12 pp.).—The single potential of aluminium was measured in a  $\frac{1}{2}$ *M*-solution of aluminium chloride at the ordinary temperature. The highest value obtained with unamalgamated aluminium was 0.32 volt, and with amalgamated aluminium, 1.00 volt. The mercury removes the coat of resistant oxide. In the first few seconds after immersion the value

1.09 decreases rapidly to 1.04—1.07, owing to formation of oxide over the amalgam. It was shown that the potential measured is actually that of the aluminium, and not that of an aluminium amalgam.

CHEMICAL ABSTRACTS.

**The Potential Necessary for the Electrolysis of Solutions of Iron.** W. ALBERT NOYES, Jun. (*Compt. rend.*, 1919, 164, 971—973).—The minimum potential necessary for the electrolysis of a solution of a ferrous salt between electrodes of electrolytic iron is 0.66 volt at 20°; this value diminishes 0.007 volt for each degree rise in temperature up to 110° when it attains a minimum, and rises again with further rise in temperature.

W. G.

**Electrical Endosmosis of Molten Sodium Chloride in Carbon.** WA. OSTWALD (*Kolloid Zeitsch.*, 1919, 25, 115—116).—When molten sodium chloride is electrolysed between carbon electrodes there is scarcely any evolution of chlorine or formation of sodium unless special conditions are established, but the negative electrode increases in volume and is partly destroyed. On cooling and treating with water the electrode falls to powder, whereas the positive electrode is unaffected either during the electrolysis or on treatment with water. The behaviour is due to the cataphoresis of the molten sodium chloride.

J. F. S.

**Heusler's Alloys.** O. VON AUWERS (*Zeitsch. anorg. Chem.*, 1919, 108, 49—69).—The opinion was expressed by Heusler that the alloys of the aluminium-manganese bronze series owe their ferromagnetic properties to a compound of the form  $(AlM_3)_x$ , where  $M_3$  represents an isomorphous mixture of manganese and copper. Whether the magnetism is to be attributed to simple molecules  $AlM_3$ , to complexes, or to a particular crystal lattice remained obscure. The phenomena attending the so-called ageing of these alloys have an important bearing on the constitution of their ferromagnetic constituent. The cast alloys have weak magnetic properties, and have to undergo the ageing process, that is, prolonged heat treatment at temperatures between 100° and 300°, to develop their full magnetic power. One effect of this treatment is to raise the magnetic transition temperature along a curve similar to a magnetisation curve. When magnetisation is plotted against time of ageing for different field strengths, a series of curves is obtained, of which those for lower field strengths show a sharp maximum with a subsequent fall to a constant magnetisation. In the curves for high field strengths the maximum is flattened out and the corresponding point is followed by a gradual rise in magnetisation as the time of ageing increases. The ageing process appears to involve two superimposed molecular changes. The author considers that at the magnetic transition point the magnetic particles become dissociated. On quenching from about 600° the alloy contains very few magnetic molecules. By slow cooling or by the ageing process the particles again become associated and the magnetisation and coercive force

both increase. With low field strengths the coercive force, that is, the intermolecular force, predominates over the magnetising force, and this explains the maximum in the above-mentioned curves. The highest point of the magnetisation curve is reached when the coercive force is a maximum, that is, when the maximum number of magnetic particles are present. The coercive force depends on the temperature of ageing, and reaches a maximum with temperatures from  $190^{\circ}$  to  $260^{\circ}$ . Above this temperature, it falls off rapidly, presumably because the dissociation of the particles has then commenced.

E. H. R.

**Some Fusion Curves, the Condition Diagram of Resorcinol and the Condition Diagrams of some Cryohydrates.**

WALTER DENECKE (*Zeitsch. anorg. Chem.*, 1919, 108, 1—43).—The pressure-temperature fusion curves of betol, triphenylmethane, erythritol, guaiacol, salol, and benzoic anhydride, all substances of low crystallisation velocity, have been determined experimentally by Tamman's method, which consists in heating a quantity of the substance under pressure and plotting the temperature-pressure curve. When fusion commences, the curve changes direction owing to a rapid increase in pressure, and the ordinates of the point at which the change of direction starts give the temperature of the melting point and the corresponding pressure. From a number of such observations at different pressures the fusion curve is plotted. The apparatus used was that described by Tamman (*Kristallisieren und Schmelzen*, 1903, 195). In each case the curve can be represented by an equation of the form  $t = t_{p=1\text{Kg}} + ap - bp^2$ , in which  $a$  and  $b$  are constants and  $p$  is the pressure at the fusion point  $t$ . All the curves are smooth, and show no evidence of polymorphism in the substances examined, although betol, triphenylmethane, and erythritol are all known in two or more crystalline modifications.

The same experimental method was applied to the study of the transition between the two forms of resorcinol. The transition of pure resorcinol is extremely slow, but is accelerated by the addition of xylene. In presence of xylene, as the temperature is raised, the pressure begins to fall when the transition commences, the fall being most marked with 1% of xylene. The more xylene there is present, the lower the temperature at which the transition begins. Increasing pressure lowers the transition temperature, but also lowers the transition velocity.

To investigate the separation of different forms of ice from cryohydrate solutions, such solutions of sodium chloride, potassium chloride, ammonium chloride, sucrose and magnesium bromide were studied by cooling under pressures up to 3000 kilos. per sq. cm. down to about  $-70^{\circ}$  and plotting the temperature-pressure curves. The regions of the equilibrium diagram of water in which the ice forms I, II, and III' are stable were thus included. In the ice I field, this form generally separated, but once, from a sodium chloride cryohydrate solution, a form was obtained which appeared to be a less stable form of ice I, and twice, from a magnesium

bromide solution, a more stable form of this group separated. At pressures above 2400 kilos. ice III' was always obtained from sodium chloride solutions, although this is the ice II region. From potassium chloride solutions sometimes ice II and sometimes ice III' was obtained, and from ammonium chloride generally ice V. From sucrose solution ice III' usually separated, but on one occasion a denser form, probably the most stable form of ice II, was observed. When ice I first separated and the pressure was raised subsequently, ice III' was formed, except in the case of magnesium bromide, where the pressure was raised to 3000 kilos. without inducing transition into a denser form of ice. The position of the transition curve of forms I and III' is not changed through the presence of the salts. The salts are therefore not appreciably soluble in these forms of ice.

E. H. R.

#### Vapour Pressures of Mercury in the Range 120–250°.

ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1919, **41**, 1783–1787).—A method is described for the measurement of low vapour pressures, involving the use of two McLeod gauges, hot and cold respectively. The method has been used to determine the vapour pressure of mercury at 121·8°, 150·0°, and 191·5°. The following values are found in mm. of mercury: 121·8°, 0·829 mm.; 150·0°, 2·802 mm.; and 191·5°, 13·02 mm. It is shown that the equation connecting vapour pressure and temperature over the temperature range 250–453° (A., 1910, ii, 1037) may be employed without modification of its constants over the range 120–250°.

J. F. S.

#### Rectification by Adiabatic Condensation without Expansion.

E. CHENARD (*Bull. Soc. chim.*, 1919, [iv], **25**, 546–552).—

As a result of a series of distillations of alcohol-water mixtures through a special apparatus designed (1) to remove from the vapour any liquid transported in the vesicular state, (2) to effect a preliminary partial condensation of the vapour and collection of the condensed portion, it is shown that the law of correspondence between the strengths of liquids and vapours in contact, in a rational process of condensation, is almost identical with the law of fractionation by vaporisation. The process of enrichment of the vapour by means of partial condensation is capable of being very useful and also very simple in its working. Starting with a vapour containing 35% of alcohol, it was found possible by fragmentary condensation, in six stages, of about 54% of the initial weight, to obtain a vapour containing 64% of alcohol. At the same time, the six fractions would, on boiling, give vapours richer than the initial vapour.

W. G.

**Distillation in a High Vacuum.** J. Houben (*Ber.*, 1919, **52**, [H], 1460–1462).—The principle of the method has already been described by Erdmann (A., 1904, ii, 20). A high vacuum is attained by means of an ordinary water pump through filling the



apparatus with carbon dioxide and condensing it in a suitable receiver by liquid air. The new improvement consists in letting the carbon dioxide enter in a continual stream through a fine capillary below the liquid, so as to prevent uneven boiling. A pressure of 0.12 mm. is easily maintained.

J. C. W.

**Comparative Investigation of the Efficiency of Still-heads of Various Types.** J. FRIEDRICH (Zeitsch. angew. Chem., 1919, 32, 340-344).—In order to test the efficiency of different types of still-head, a mixture of equal quantities of benzene and toluene was distilled at a constant speed, which was controlled by means of a vapour pressure regulator between the still-head and the condenser. The temperature within the still-head and the volumes of distillate were taken at regular intervals, and the results are given in tabular form. It was found that still-heads containing glass beads or fragments were the most effective, whilst for the distillation of larger quantities of liquid the use of a long tube, as in Hempel's apparatus, is best. Winssinger's modification of Hempel's still-head gives good results with liquids boiling below 100°, whilst a modification of Plücker's apparatus combines the advantages of Winssinger's dephlegmator and Ekenberg's rectifying apparatus. In the case of small amounts of liquids, Linemann's apparatus gives the best results. [See also *J. Soc. Chem. Ind.*, 1919, 964A.]

C. A. M.

**Heat of Hydration of Gaseous Ions.** K. FAJANS (*Ber. deut. physikal. Ges.*, 1919, 21, 549-558).—The heat of solution of a salt in water is regarded as made up of two quantities, (i) the heat absorption necessary for complete dissociation of the salt into gaseous ions, and (ii) the heat developed in the solution of these ions in water. The latter quantity is termed the heat of hydration of gaseous ions. From a knowledge of  $L$ , the heat of solution of a binary salt, and  $U$ , the total energy change, the author shows that the heats of hydration of the gaseous ions may be calculated. Employing this method, the following values, in kilogram cal. per gram-ion, are calculated:  $H^+$ , 362;  $Li^+$ , 210;  $Na^+$ , 203;  $K^+$ , 182;  $Rb^+$ , 173;  $Cs^+$ , 174;  $Tl^+$ , 182;  $Ca^{++}$ , 475;  $Cl^-$ , -23;  $Br^-$ , -32;  $I^-$ , -43. The values are claimed to be accurate within 6 units in the case of cations and 10 units in the case of anions.

J. F. S.

**Heat of Ionisation and Chemical Constitution.** E. OLIVERI-MANDALA (*Gazzetta*, 1919, 49, ii, 176-180).—With a few exceptions, weak electrolytes exhibit heats of ionisation differing little from a mean value of 500 cal. and attempts have been made to explain the exceptional values by means of the chemical constitution of the electrolytes concerned. Thus, according to Bauer (*A.* 1897, ii, 546), the magnitude of the heat of ionisation may indicate the union of the hydrogen of an electrolyte to a nitrogen rather than to an oxygen atom, whilst Hantzsch employs it to diagnose

the presence in solution of a pseudo-acid, and Jones considers that anomalous heats of ionisation support his hydrate theory. Further, the high heats of ionisation shown by water and hydrofluoric acid have been explained as the result of a process of depolymerisation.

The author points out that the heat of ionisation, calculated from the heat of dissociation, depends on the other constants of the equilibria existing in solution and on the thermal effects of these equilibria, so that the magnitude of the heat of ionisation of a substance cannot serve as a physico-chemical means of investigating either intramolecular changes of electrolytes in solution or transformations of other character. The particular cases of a pseudo-acid and of hydrofluoric acid are considered, and an equation identical in form with, but different in signification from, that found by Lunden in the case of ammonia is derived (compare A., 1916, ii, 367).

T. H. P.

**Differences in the Heats of Combustion and in Other Properties of Isomeric Forms of Compounds of the Type Tartaric Acid-Mesotartaric Acid.** E. BERNER (*Tidskrift Kemi*, 1919, **16**, 97--110, 118--128). The differences in the heat of combustion, density, solubility, and sublimation point were ascertained for the isomeric forms of tartaric acid, phenylglyceric acid, and hydrobenzoin. For the heat of combustion, the units in the following are kilo. cal. per gram-mol. The methyl ester was used in place of tartaric acid. Tartaric acid in the *meso*-form gave 623.2 Cal., in the *d*-form 621.8 Cal. Correcting for the difference in the heat of solution, the difference between these two is 2.6 Cal. Corresponding stereoisomeric forms of phenylglyceric acid (m. p.'s 122° and 141° respectively) gave 1011.2 and 1004.2 Cal., a difference of 5.4 Cal. after correcting for the heat of solution. In hydrobenzoin and *isohydrobenzoin* the relations are reversed, the stereoisomeride corresponding with *d*-tartaric acid giving a smaller heat of combustion (1723.2 Cal.) than the other isomeride (1728.0 Cal.). The difference after correcting for the heat of solution is 4.5 Cal. *r*-Tartaric acid gave 0.5 Cal. more heat than did the *d*-isomeride. The author concedes that this may have been an experimental error, but cites Ossipoff (*Compt. rend.*, 1889, **109**, 475), who also noted a difference in the heats of combustion of these two isomerides, namely, 619.5 and 618.5 Cal. Attention is directed to the fact that the first four substances mentioned above are derived from the following acids, with heats of combustion as indicated: maleic (329.6), fumaric (320.7), *allocinnamic* (1047.6), and *cinnamic* (1042.3 Cal.), respectively, and that in the transformation the relative rank as to energy is not altered. In isomeric forms greater solubility and lower m. p., sublimation point, density, and molecular volume in solution are associated with the isomerides of higher heats of combustion. The tartaric acids are an exception to this rule, as are also maleic and fumaric acids, from which the tartaric acid isomerides may be derived.

CHEMICAL ABSTRACTS.

**The Benzene [Formula] Problem. II.** A. VON WEINBERG (*Ber.*, 1919, 52, [B], 1501—1508).—From the data for the heats of combustion of various hydrocarbons, a discussion of the kinetics of benzene and related compounds is developed.

In the first place, it is shown that the heat of combustion of a saturated hydrocarbon,  $C_nH_m$ , can be expressed very nearly by the term  $96n + 30m$  Cal., that is, each carbon and each hydrogen atom contributes a constant quantity. This is developed from two series of data. (1) Let  $x$  = the contribution of the carbon atom, and  $y$  that of the hydrogen. Then, in the case of ethane,  $2x + 6y = 370.9$ , and in the case of propane,  $3x + 8y = 526.7$ , whence  $x = 96.5$  and  $y = 29.65$ . (2) The increment for the  $\cdot CH_3$  group is known to be 156 Cal., and the average heat of combustion of the isomeric octanes is 1299.9 Cal. (Richard and Jesse, A., 1910, ii, 269). To the latter value should be added the latent heat of vaporisation, which is 8.09 Cal. Then  $x + 2y = 156$  and  $8(x + 2y) + 2y = 1308$ , whence  $x = 96$  and  $y = 30$ . Two consequences follow from this additivity. First, the energy of the rupture of a C-H linking must be the same as that of a C-C bond, and, secondly, the heat of combustion of a carbon atom in gaseous carbon must be the same as that of a carbon atom in a simple hydrocarbon vapour. Now it is quite remarkable that the above value, 96, is very nearly the same as the heat of combustion of solid carbon, from which it appears that in the vaporisation of carbon there is very little force of cohesion to overcome. This is in accordance with the view that carbon is mono-atomic in the diamond, as revealed by a study of the space-lattice and diminution of the specific heat at low temperatures.

The heat of dissociation of the C-H or C-C linking can be calculated as follows. The heat of combustion for one H in hydrocarbons is 30, but for two H atoms in hydrogen gas it is not 60, but 67.5, that is, the heat of dissociation of the C-H bond is less than that of H-H by 7.5. The value used by Nernst for the heat of dissociation of hydrogen is 100 Cal., from which it follows that the required quantity is 92.5 Cal.

The additional energy of the molecule due to one or more double linkings may be calculated by subtracting the value for the term  $96n + 30m$  from the heat of combustion. From the values for ethylene, propylene, and hexylene, it appears that the increment due to the single ethylene linking is equivalent to about 30 Cal. For  $\Delta^6$ -hexadiene, however, it is only 16.3, instead of twice 30, and for  $\epsilon$ -methyl- $\Delta^3$ -hexadiene it is only 20.8. This is due to the fact that the oscillations set up by one double bond interfere with and restrict those of the other. The case of the conjugated linkings is most interesting, for this really represents the energy of vibration of three pairs. Now if benzene has three conjugated double bonds, the energy of six oscillating pairs will have to be reckoned, that is,  $2 \times 16.3 = 32.6$  Cal. Actually, the additional energy given out by benzene, above that calculated from the term  $6 \times 96 + 6 \times 30$ , is 32.7 Cal. if Roth's value for the heat of combus-

tion is correct (A., 1915, ii, 146), or 30.3 if Richards and Barry's number is accepted (*ibid.*, 421). The oscillation energy of each carbon atom in benzene is therefore 5.4 or 5.05 Cal., that is, about one-third of the energy of an ethylenic carbon atom. This agrees with the fact that the oscillation frequencies are slower in benzene and approach those of the visible spectrum. From the data available for naphthalene and anthracene, it appears that the average oscillation energy for one carbon atom is again about 5 Cal. Formulae are given with which it is possible to discuss the amplitudes and frequencies of the oscillations of the  $\alpha$ - and  $\beta$ -carbon atoms in these compounds.

The excess energy in the case of *cyclohexane*, that is, the energy due to ring formation, is 8.2 Cal. This rises to 23.6 when one ethylene linking is also present (*cyclohexene*), to 38.6 when two are present (*cyclohexadiene*), but is 32.7 in the case of benzene.

J. C. W.

**New Gas Pyknometer.** K. KLING and L. SUCHOWEAK (*Metan*, 1917, 1, 37—42; from *Chem. Zentr.*, 1919, iv, 437—439).—The authors describe a new form of gas pyknometer suitable for use with small quantities of gas and for the estimation of density without using a current of gas or a pump. The principle of the apparatus depends on the observation that carefully purified and dry mercury flows quantitatively from the well-cleaned apparatus. A single filling of the pyknometer by mercury suction leaves the vessel quantitatively filled with the gas. A further feature is the complete absence of stopcocks. The apparatus is very fully illustrated in the original.

H. W.

**Table for the Correction of Volumes of Gases.** W. OSTWALD (*Zeitsch. angew. Chem.*, 1919, 32, 359—360).—A calculation diagram for the correction of gas volumes to normal temperature and pressure, including correction for the tension of aqueous vapour, may be constructed by plotting the values for barometer readings and the ascertained correction factors on two parallel logarithmic scales, joining the respective points on these scales by a straight edge and marking points between them to represent the corresponding temperatures. The temperature scale thus plotted includes the aqueous vapour correction, and will be found to take the form of a straight line parallel to the other two. The barometric and temperature scales can then be used for finding the corresponding correction factor without calculation, and the multiplication of the observed volume by this factor to obtain the corrected volume may be performed graphically, in the same manner by constructing two other logarithmic volume scales on the same diagram.

J. F. B.

**Molecular Volumes.** W. HERZ (*Zeitsch. anorg. Chem.*, 1919, 108, 226—230).—For a number of homologous series of organic compounds, the author has compared the "true" molecular volumes given by the expression  $V = D - 1, D + 2, M/d$ , where  $D$  is the

dielectric constant and  $d$  the density, with the molecular volume at absolute zero,  $V_0$  (A., 1919, ii, 220). In general, both  $V$  and  $V_0$  increase with the molecular weight, although acetic acid shows an abnormally high value for  $V$  in the series of homologous acids. The molecular volumes at absolute zero are greater than the true molecular volumes, and the difference increases with the molecular weight. In the benzene series, the ratio  $V/V_0$  is a constant, and the same is true in the paraffin series from hexane to decane. In the fatty acids, the alkyl formates, and alkyl acetates the ratio decreases as the series is ascended, but it approximates to a constant value in the higher members of each series. In the early members of these three series, the difference between the two molecular volumes is very small, indicating that the substances have a very compact structure. In the alcohol series, from methyl to amyl alcohol, the true molecular volume appears to be actually greater than the molecular volume at absolute zero. The abnormality becomes smaller with increasing molecular weight, and disappears beyond amyl alcohol. It is probably due to association in the alcohols, as a similar abnormality is found in the case of formic acid.

E. H. R.

**Molecular Volumes of Liquid Organic Compounds.** HUGO KAUFFMANN (*Zeitsch. Elektrochem.*, 1919, 25, 343-351).—The author has examined the molecular volumes of a large number of organic compounds, using the experimental data of Lossens (A., 1890, 323) for the purpose. It is shown that the molecular volume at the boiling point is not suitable for the investigation of regularities or for the calculation of atomic volumes. The molecular volume at a given temperature brings important regularities to light which run parallel with other physical properties. The density in homologous series of organic compounds approaches limiting values characteristic for each temperature: thus, at  $0^\circ$   $D=0.8752$ ; at  $20^\circ$   $D=0.8616$  as a limit. If the density of the first member of an homologous series is smaller than the limit, then the density in that series increases with increasing molecular weight, but should the density of the first member be larger than the limit then the density falls with increasing molecular weight in that series. The author recognises "Accumulation phenomena." This is the name applied to the combination of several groups or atoms with a given atom. Accumulation increases the molecular volume, and this mainly in the third and fourth stage. This is equally true for mixed and similar accumulation. Atoms or groups which bring about exclusively large increases in the molecular volume are termed *Eurogens*, and the accumulation phenomenon itself is termed *Eurogenism*. Carboethoxyl-, chlorine, nitro- and cyanogen groups are strong eurogens. The strength of the eurogens named increases in the order given; and other carbonyl-containing groups are stronger than the carboethoxyl group. The ethoxyl and phenyl groups are weaker than the carboethoxyl group, and the  $-\text{CO}\cdot\text{O}-$  group is a bivalent eurogen. Of the alcohol radicles,

only the methyl group has eugenenic properties. This peculiarity of the methyl group has the effect that the second member of every homologous series shows a slight irregularity in the approach to the limiting value. The molecular volume of isomeric aliphatic compounds is controlled largely by the eugenenic character of the methyl group. In substituted derivatives the eugenenic influence of the methyl group is combined with its substitution influence. The difference between the molecular volumes of isomerides is a measure of the eugenism. In accumulation of the second stage the methyl group may lose some of its activity, since methyl groups when they are combined with neighbouring carbon atoms, acting as accumulation centres, reduce the molecular volume. A similar state of affairs is shown to exist in silicon compounds where the silicon atom is acting as the accumulation centre.

J. F. S.

**A Thermodynamic Proof.** ARRIGO MAZZUCHELLI (*Atti R. Accad. Lincei*, 1919, [v], 28, ii, 47—51).—Lewis ["System of Physical Chemistry" (2nd Ed.), II, 140] directs attention to the divergent results attained by two proofs, both apparently unobjectionable, of the relation between pressure and equilibrium constant in dilute solutions. One of these proofs is due to Planck, who arrives at formula 220 of his "Thermodynamik" (3rd Ed.), and the other to Rice (*Trans. Faraday Soc.*, 1917, 12, 318), who derives the formula  $dP \log K = (V_1 - V_2)/RT$ , where  $K$  is the equilibrium constant (constant of formation of the final system referred to concentration by volume) and  $V_2 - V_1$  the variation in volume due to the integral transformation of the initial system into the final one. The author introduces certain modifications into Rice's system and shows that Rice's cycle then leads to Planck's formula, although he does not claim to have proved that such modifications are justified.

In the cases which up to the present have been subjected to experiment, a compression, besides altering the equilibrium constant in the sense favouring the system with a less total volume, that is, in accordance with the Le Chatelier-van't Hoff principle, also causes a certain increase in the concentration by volume, owing to the compressibility of the solution. Such increase in concentration, although without direct influence on the equilibrium constant, yet favours as a rule the system with the less number of molecules, of which it increases the relative quantity; in the experimental measurements, such increase figures, therefore, as a further variation of the equilibrium constant, and it should be taken into account by any rigorous theoretical formula.

T. H. P.

**Surface Tension and its Relationship to Other Properties of Liquids.** W. HERZ (*Zeitsch. physikal. Chem.*, 1919, 93, 607—612).—A theoretical paper in which the author examines the values of the surface tension, molecular surface energy, the temperature-coefficient of the molecular surface energy, and the molecular association of a number of organic compounds in their relations to the number of carbon atoms in the molecule. It is shown

that in homologous series the surface tension decreases with increasing number of carbon atoms, whilst the molecular surface energy becomes larger. The temperature-coefficient of the molecular surface energy increases in homologous series at the same temperature with the number of carbon atoms. From this it is deduced that the tendency to association decreases as the number of carbon atoms increases. Richard's rule that the compressibility is inversely proportional to the surface tension is examined in a large number of cases and confirmed. The compressibility is larger the fewer the molecules in unit volume, that is, the larger the molecular diameter.

J. F. S.

**The Technique of the Estimation of the Viscosity of Organic Colloids.** E. ROTHLIN (*Biochem. Zeitsch.*, 1919, 98, 34—92).—The superiority of the "capillary" methods over the "damping" methods in the estimation of the viscosity of fluids is discussed. The author examined the viscosity of various emulsoids under different pressures by means of Hess's viscometer (capillary principle). Emulsoids, like gum arabic, soluble starch,  $\beta$  gelatin, and casein, have been found to obey Poiseuille's law. Others like gelatin, egg-white, insoluble starch, agar, and soap have shown a deviation from the above-mentioned law as the pressure was diminished. In the case of one of these colloids, namely, gelatin, higher temperatures, the addition of hydrochloric acid, sodium hydroxide, sodium chloride of suitable concentrations as well as alcohol prevented this deviation. Two pressure regions in the viscosity of these emulsoids could be differentiated, the "upper" region, in which the colloids practically obeyed Poiseuille's law, and the "lower" region, in which they deviated from it. This deviation under low pressure the author attributes to the cohesive forces of the particles. The importance of the pressure factor and the dimensions of the capillaries in the estimation of the viscosity of fluids is pointed out. Hess's viscometer fulfils these requirements.

S. S. Z.

**Influence of the Red Blood Corpuscles on the Internal Friction of Blood.** KARL BRCK (*Kolloid Zeitsch.*, 1919, 25, 103—110).—The viscosity of human blood has been measured with the object of ascertaining the relationship between this value and also of testing the Einstein relationship,  $K' = K(1 + 2.57)$  (*Ann. Physik*, 1906, 19, 289; 1911, 34, 591). It is shown that the  $\alpha$  value depends on the number of suspended particles in the sense that at small concentrations the influence on the viscosity is smaller, and at high concentrations larger, than would be the case with a constant value of  $\alpha$  (2.5). This is in keeping with previous results obtained for emulsions of oil (*A.*, 1904, ii, 646; 1907, ii, 232). It follows, therefore, that the influence of a non-rigid particle on the viscosity cannot be determined either by Einstein's formula or by any simple application of the mixture rule.

J. F. S.

**Wo. Ostwald's Rule Connecting Colour and Degree of Dispersion.** E. WEDEKIND and H. RHEINBOLDT (*Ber.*, 1919, 52, [B], 1794).—A note to remove a possible misconception of the authors' views on Ostwald's theories (*A.*, 1919, ii, 270).

J. C. W.

**The Effect of Salts on the Vapour Pressure and Degree of Dissociation of Acetic Acid in Solution. An Experimental Refutation of the Hypothesis that Neutral Salts Increase the Dissociation Constants of Weak Acids and Bases.** JAMES WILLIAM MCBAIN and JAMES KAM (*T.*, 1919, 115, 1332—1346).

**Resolution of the Acid Salts of Dicarboxylic Acids into the Free Acids and the Normal Salts.** JOH. PINNOW (*Ber.*, 1919, 52, [B], 1662—1667).—The method of estimating the first and second dissociation constants of dibasic organic acids proposed by McCoy (*A.*, 1908, ii, 466, 467), namely, by extracting solutions of the acid salts with ether and determining the partition coefficient of the acid, has been tested by Dieckmann and Hardt (*A.*, 1919, 52, 326), who found that the ratio  $k_1:k_2$  is not always independent of the concentration, as it should be. They consequently formed the opinion that there are sources of error inherent in the method itself. Some of these are now discussed.

In the first place, the determination of the partition coefficient of the acid will be influenced by association and ionisation. As the solution becomes more dilute, the associated molecules become fewer and the rate of extraction rises to a constant value (see *A.*, 1915, ii, 679). Then it begins to fall unless some sulphuric acid is added to prevent ionisation. Another factor is the "salting out" effect of the normal and acid salts, which is, of course, less in dilute solutions than in concentrated ones. The question whether any of the metallic salt is extracted by ether in the Partheil-Rose apparatus used in these investigations has been tested in the case of sodium and potassium hydrogen oxalates and potassium tetroxalate but the quantity is found to be quite negligible.

The relationship between free acid ( $l$ ), acid salt ( $m$ ), and normal salt ( $d$ ), as expressed in the term  $m^2 f \cdot d$ , is independent of the nature of the alkali in the case of succinic acid.

J. C. W.

**Structure of the Capillary Layer. III.** G. BAKKER (*Zeitsch. physikal. Chem.*, 1919, 93, 570—584. Compare *A.*, 1915, ii, 614; 1916, ii, 553).—The capillary layer is regarded as a film which has been formed by and between the liquid and gaseous phases without changing the total mass of these two phases. If  $n$  is the total number of molecular layers of gas and liquid which go to form the capillary layer consisting of  $R$  new layers, then  $R = \eta n$ , where  $\eta$  is a characteristic constant. Making use of the Laplace formula for molecular pressure,  $Q = a^{-2} (\sqrt[3]{p_1} + \sqrt[3]{p_2}) \cdot \sqrt[3]{M/N} \cdot (p_1 - p_2)^{2/3} H$  or  $\sqrt[3]{p_1} + \sqrt[3]{p_2} \cdot \sqrt[3]{M/N} \cdot r_1(p_1 - p_2) H \cdot T \cdot (ds/dt)$ , in which  $a$  is



the Laplace constant,  $\rho_1$  the density of the liquid,  $\rho_2$  the density of the vapour,  $M$  the molecular weight,  $N$  the Avogadro number,  $H$  the surface tension,  $r_i$  the internal heat of vaporisation. Both formulæ are identical, since the equation  $p = Tf(v) - a/v^2$  has been used in developing them. The equation for the number of layers in the capillary layer therefore becomes

$$R = 1 + Q/q + \sqrt{2Q/q + Q^2/q^2}.$$

If, however, the more exact formula of Clausius is used for the molecular pressure,  $Q = \frac{1}{2}(\sqrt{\rho_1} + \sqrt{\rho_2})\sqrt{M/N} \cdot r_i(\rho_1 - \rho_2)/(1 - T/a \cdot da/dt) \cdot (1 + \beta\rho_1)(1 + \beta\rho_2)$ . By means of these formulæ, the number of layers in the capillary layer, the thickness of the layer, and the number of molecular layers of vapour and liquid going in its formation have been calculated for carbon dioxide, benzene, and ethyl ether. The following values are obtained at the temperatures given:

*Carbon Dioxide.*

$t$	-25°	-10°	0°	10°	20°	28°	30°
$R$	4.8	5.4	5.4	6.9	8.8	13.3	28
$n$	4.3	5.0	5.1	6.6	8.6	13.2	28
$\zeta$	2.6	2.9	2.9	3.7	4.8	7.2	15 $\mu$

*Benzene.*

$t$	5.4°	50°	80	100°	150°	200°	250°	275°	280
$R$	3.8	5.27	5.0	5.23	5.35	5.8	8.3	12.7	17.8
$n$	2.9	4.3	4.2	4.5	4.7	5.4	8.0	12.4	17.7

*Ethyl Ether.*

$t$	0°	20°	50°	80	120°	170°	190°	193
$R$	4.2	5.1	5.1	6.1	7.0	9.6	18.4	24.5
$n$	3.4	4.2	4.4	5.4	6.4	9.3	18.2	24.5

The present results are compared with, and criticised in connexion with, the results published in previous papers (*loc. cit.*).

J. F. S.

**The Molecular Theory of Solution.** SAMUEL CLEMENT BRADFORD (*Phil. Mag.*, 1919, [vi], **38**, 696-705). The theory of solution is considered from the point of view of the attractions of the solute and solvent particles for themselves and for one another. Whereas on Traube's "cohesion pressure" theory of solution, wherein cohesion pressure signifies the attraction of solute and solvent, the solubilities of organic liquids follow the order of their cohesion pressures, the solubilities of solid substances are in the reverse order. On the basis of the kinetic theory, the electronic theory leads to an expression of the form  $f = M_v^2/r_v^4 - 2M_sM_v/r_{sv}^4 + M_s^2/r_s^4$ , where  $M_v$  and  $M_s$  are respectively the moments of atomic doublets in solute and solvent, and  $r_v$ ,  $r_{sv}$ , and  $r_s$  the respective distances between the centres of two solvent doublets, a solute-solvent doublet, and two solute doublets for the force initially tending to prevent solution.

This relation, combined with that expressing the ratio of the number of molecules in unit volume of the liquid solvent to the number in unit volume of the solid solute, is employed to deduce a number of conclusions relating to solution. Thus, the more a solute increases the surface tension of the solvent, the less its solubility. In the case of solutes which increase the surface tension of the solvent, the order of the compressibilities of their solutions will be the same as that of the solubilities of the respective solutes. Salts have a greater solubility, the larger their respective molecular volumes. It is shown that in accordance with the theory developed, the solubilities of sulphur dioxide, hydrogen sulphide, nitrous oxide, carbon dioxide, carbon monoxide, oxygen, nitrogen, and hydrogen are greater in alcohol than in water, and that, moreover, the difference of solubilities in the two liquids increases as the molecular cohesion of the gas diminishes.

J. S. G. T.

#### Thermochemical Proof of Born's Crystal Lattice Theory.

K. FAJANS (*Ber. deut. physikal. Ges.*, 1919, **21**, 539—548).—The author has calculated the energy of formation of gaseous ions from the crystalline salt by means of the known experimental values for the heat of solution of calcium chloride, calcium iodide, lithium iodide and chloride. These results are compared with the corresponding values calculated on the basis of Born's cubic atom model theory (A., 1919, ii. 188). It is shown that the two sets of values are in excellent agreement, and that they furnish a confirmation of this theory.

J. F. S.

#### Colloid Synthesis by means of Oscillating Arcs.

GÖSTA BJÖRJESON and THE. SVEDBERG (*Kolloid Zeitsch.*, 1919, **25**, 154—158).—Using capacities in circuit, arcs of various metals have been struck in alcohol when the disintegrated metal forms colloidal solutions. In the experiments with a capacity of  $12.8 \times 10^{-3}$  MF and a current of 1.5 amperes colloidal solutions of antimony, lead, bismuth, zinc, gold, platinum, silver, copper, aluminium, and cadmium have been obtained. By this method the colloidal metal is produced more rapidly than by the earlier Svedberg method, in some cases four times as rapidly. The stability of the sols is fairly great, although a certain amount always separates, but even then the bulk of the metal remains in solution. Gold and platinum are exceptional, being very unstable.

J. F. S.

#### The Effect of Organic Acids and their Amino-compounds on the Hydration of Agar and on a Biocolloid.

D. T. MACDOUGAL and H. A. SPOHR (*Proc. Soc. Expt. Biol. Med.*, 1918, **16**, 33—35).—Three groups of substances were selected: (1) succinic acid and its amino-compound, aspartic acid, both of which are dibasic, and its amide, asparagine, which is monobasic; (2) acetic acid and glycine, which are monobasic; (3) propionic acid and alanine, also monobasic, their action on the swelling of sections of agar and a mixture of 8 parts of agar and 2 parts of oat protein being

studied. Equimolecular concentrations of the three organic acids present small divergence of effect on agar and more positive differences in agar-protein. Agar swells more in succinic acid than in its amino-compound, but reverses this relation with the other two acids and their amino-compounds. The agar protein biocolloid showed greater hydration in the amino-acids than in the related organic acids, greater even than in distilled water. Glycine facilitates hydration in all concentrations above 0.01*M* in both agar and agar-protein, and also in agar-gelatin. The amide, asparagine, induces a maximal hydration, greater even than that possible in agar in distilled water and very high at all concentrations.

#### CHEMICAL ABSTRACTS.

**Protective Colloids. 2nd Series. Cetraria Islandica as Protecting Colloid. IV. Colloidal Copper.** A. GUTBIER and E. SAUER (*Kolloid Zeitsch.*, 1919, **25**, 145—153. Compare A., 1916, ii, 231, 303).—Extract of Iceland moss has been prepared in three ways: *A*, by extracting the moss with distilled water; *B*, by washing the moss first with dilute potassium carbonate and then extracting with water; *C*, the product *B* is rubbed with distilled water and then stirred with water and dialysed. These three extracts were used as protective colloids in the preparation of colloidal copper solutions from ammoniacal copper sulphate solutions and hydrazine hydrate. The copper sols are so very sensitive that it was possible to test the three extracts as to their protective action. Extract *C* is by far the most efficient, and *B* is far superior to *A*. The sols produced, using 0.1—0.05% of cetraria extract, are fairly stable, but deposit a dark red precipitate in fourteen days, which is reversible. Colloidal copper solutions which by transmitted light are clear red and slightly turbid by reflected light on keeping, deposit fine-grained, irreversible precipitates, but those which are bright red in both lights deposit completely reversible precipitates. The preparation of the solid colloid may be effected by adding  $\frac{1}{2}$ —1 volume of alcohol. The colloids thus obtainable are not very rich in copper, the limit of absolute reversibility being reached with a copper content of 13.43%.

J. F. S.

**Relationship between Shrinking and Diffusion Structure in Tanned (Hardened) Gelatin Jellies.** W. MOELLER (*Kolloid Zeitsch.*, 1919, **25**, 101—109).—The structures of hardened jellies produced by shrinking and by the diffusion of solutions into the jellies have been investigated. It is shown that the structures, produced by the diffusion of solutions of sodium hydroxide into gelatin-sodium chloride jellies which have been hardened by formaldehyde, are due to changes in the internal structure of the micellar envelope. The thin, tanned layer attaches itself closely to the underlying coarse structure, and completely follows the direction of the coarser structure. Under tension, shrinkage lines appear in radial directions from the diffusion centre, and concentric ring systems are produced by the contractions of the micellar envelope.

Irregularities may be caused by the passage of drops of alkali hydroxide solution through the fine pores of the surface film.

J. F. S.

**Studies in Catalysis. Part XII. Catalytic Criteria and the Radiation Hypothesis.** WILLIAM CUDMORE McCULLAGH LEWIS (T., 1919, 115, 1360—1366).

**Calculation of the Ammonia Gas Equilibrium.** EDUARD MAURER (*Zeitsch. anorg. Chem.*, 1919, 108, 273—302).—A comparison is made of the results obtained for the nitrogen-hydrogen-ammonia equilibrium at different temperatures and pressures by Haber and Le Rossignol and Jost (A., 1908, ii, 362, 761) respectively. It is concluded that the results of these experimenters are in full agreement, and further that the work of Jost, carried out in Nernst's laboratory, was a sufficient scientific foundation for the technical synthesis of ammonia.

E. H. R.

**The Equilibrium between Carbon, Hydrogen, and Methane.** HUBERT FRANK COWARD and STANLEY PIERCE WILSON (T., 1919, 115, 1380—1387).

**Calculation of the Temperature-coefficient of the Distribution Ratio.** F. H. MACDOUGALL (*J. Amer. Chem. Soc.*, 1919, 41, 1718—1721).—A mathematical paper in which the author derives the temperature-coefficient of the distribution ratio for succinic acid between water and ether. This value has previously been deduced by Forbes and Coolidge (A., 1919, ii, 141), but the present author points out that the mathematical expression is likely to be misleading. The present expression has the form  $dR/dt = 1/\sigma_s[(b_1 + a_1\mu_2)/(1 - a_1\mu_2) - R \cdot (B_1 + a_1\nu_2) \cdot (1 - a_1\mu_2)]$ , which is identical with that of Coolidge and Forbes. The Greek letters refer to the ether phase, and the Roman letters to the aqueous phase,  $\sigma_s$  is the mol. fraction of acid in water saturated with ether,  $b_1 = \text{Lim}(ds_1/dt)_{e_1}$ , where  $e_1$  is the mol. fraction of ether in the water layer, saturated with acid but not with ether, and  $s_1$  is the mol. fraction of acid in the water layer saturated with acid but not with ether;  $n_2 = \text{Lim}(de_2/dt)_{s_1}$ ; the meanings of the other symbols follow the same order.

J. F. S.

**Relations between Distribution Ratio, Temperature, and Concentration in System: Water, Ether, Succinic Acid.** G. S. FORBES and A. S. COOLIDGE (*J. Amer. Chem. Soc.*, 1919, 41, 1721). Compare preceding abstract, also A., 1919, ii, 141).—An acknowledgment of Macdougall's paper (*loc. cit.*) and an indication of the method by which a misinterpretation of the previous equation may be avoided.

J. F. S.

**The Propagation of Flame in Complex Gaseous Mixtures. I. Limit Mixtures and the Uniform Movement of Flame in such Mixtures.** WILLIAM PAYMAN (T., 1919, 115, 1436—1445).

**The Propagation of Flame in Complex Gaseous Mixtures. II. The Uniform Movement of Flame in Mixtures of Air with the Paraffin Hydrocarbons.** WILLIAM PAYMAN (T., 1919, 115, 1446—1453).

**The Propagation of Flame in Complex Gaseous Mixtures. III. The Uniform Movement of Flame in Mixtures of Air with Mixtures of Methane, Hydrogen, and Carbon Monoxide, and with Industrial Inflammable Gases.** WILLIAM PAYMAN (T., 1919, 115, 1454—1462).

**The Ignition of Ether-Alcohol-Air and Acetone-Air Mixtures in Contact with Heated Surfaces.** ALBERT GREVILLE WHITE and TUDOR WILLIAMS PRICE (T., 1919, 115, 1462—1505).

**The Diastatic Inversion of Sucrose: Influence of the Products of the Reaction on the Velocity of Hydrolysis.** H. COLIN and (Mlle.) A. CHAUDUN (*Compt. rend.*, 1919, 169, 849—852).—It has been shown previously (compare A., 1919, ii, 327) that the diminution in the velocity of inversion of sucrose by sucrase, due to an increase in the concentration of the sucrose, is really a linear function of the fluidity of the solution. It is now shown that the diminution in the velocity of inversion due to the presence of the products of inversion or of dextrose or levulose separately is simply a physical effect due to an increase in the viscosity of the solution. In all these cases, the velocity of hydrolysis is a linear function of the fluidity of the solutions. W. G.

**The Structure of Atoms.** A. BERTHOUD (*Arch. Sci. phys. nat.*, 1919, [v], 1, 473—496).—A résumé of recent work on this subject. W. G.

**Modification of Bohr's Atomic Model.** F. KIRCHOF (*Zeitsch. physikal. Chem.*, 1919, 93, 623—633).—A theoretical paper in which the author puts forward an hypothesis of the constitution of the atom which, although based on Bohr's hypothesis, differs in many details. The outside ring is assumed to contain 8 electrons and atoms, and never more; thus, carbon and silicon contain 4 electrons and can combine with 4 atoms, fluorine and chlorine contain 7 electrons and may combine with 1 atom, argon contains 8 electrons in its outside ring, and so is saturated and cannot combine at all. This view is in keeping with Abegg's contravalency hypothesis, and it follows that the number of electrons in the outside ring is the same as the contravalency of the element. The author suggests that the second ring, from the nucleus, containing 8 electrons and beginning with sodium, is responsible for the *K*-series spectrum, whilst the *L*-series spectrum is due to a ring with 12 electrons (third from nucleus) and commences with zinc; the *M*-series spectrum is due to a ring (fourth from the nucleus) containing 14 electrons and commencing with gold. J. F. S.

**Spectroscopic Proof of Electrical Fields on the Surface of Chemical Atoms.** J. STARK (*Ann. Physik*, 1919, [iv], 60, 196—200).—A theoretical paper in which, from a consideration of the third subsidiary series of lithium and helium, and of the conditions under which these series become visible, it is shown that electric fields are situated on the surface of the atoms. J. F. S.

**Nature of the Forces between Atoms in Solids.** RALPH W. G. WYCKOFF (*J. Washington Acad. Sci.*, 1919, 9, 565—592).—A theoretical paper in which the structure of the atom is discussed with reference to the nature of the forces operating between atoms; it is emphasised that only the arrangement of the outside electrons has a bearing on the phenomena usually described as chemical. The arrangement of the inner electrons cannot be deduced from chemical data alone. The outstanding fact is the tendency to form "closed clusters" of 8 or 16 electrons. A number of typical compounds are considered with reference to the nature of the forces producing them. All compounds lie between the two extremes of "polar" and "non-polar" compounds. A simple method of representing the type of combination in a given compound is put forward. Solid substances are classified, according to the nature of the forces of combination, into molecule-forming, polar, and valency compounds. The phenomena of adsorption, solubility, ionisation in solution, formation of complex ions, and molecular complexes are discussed from this point of view. J. F. S.

**Derivation of Chemical Relationships from the Electron Theory.** HEINRICH TERT (Zeitsch. anorg. Chem., 1919, 108, 137—160).—In a previous paper (A., 1919, ii, 330) was outlined a theory of the periodic system of the elements based on certain assumptions regarding the mode of arrangement of the electrons in the atoms. This theory is now extended to a consideration of the combination of atoms to form molecules and compounds. Since the inner electrons rotate in a series of rings as near to the equator of the atom as possible, it follows that the positive lines of force due to the positive charge of the nucleus are concentrated at the poles of the atom and attract valence electrons to this region. Combination between atoms therefore takes place at the poles of the atoms, and the electrons held in common between the combining atoms rotate in an orbit between the poles of the combined atoms. In addition to the attractive force between the valence electrons and the positive nucleus of opposing atoms, forces of attraction between the electrons of the inner rings and the positive spaces between them also come into play, and it is shown that, in the case of two atoms of a metalloid element, the net result is an attraction, whilst with two atoms of a metal a repulsion results, or a much weaker attraction. This explains why metalloids generally form polyatomic molecules, whilst the molecules of the metals are monatomic. Similar considerations explain the stability of compounds of different metalloid elements and the ionisation of salts

of the lithium fluoride type. The cause of odour in chemical compounds is traced to the oscillations of the valence electrons in their orbits between the poles of combined atoms. E. H. R.

**Mathematical Proof that the Atomic Weights are Integers when  $O=16$ .** HAWKSWORTH COLLINS (*Chem. News*, 1919, 119, 247—248).—When the elements are written down in ascending order of atomic weight, it is found that, of the first 25, 21 have values assigned to them which differ by less than 0.5% from integers. The probability that this has happened by accident is 1 in a billion. The five exceptions to this are:  $Cl=9.1$ ,  $Mg=24.32$ ,  $Ne=20.2$ ,  $Si=28.3$ , and  $Cl=35.46$ . Of these, neon need not be considered, because it is probably a mixture. If the atomic weights of the remaining elements are reduced by the same proportion, they become  $Cl=9.00$ ,  $Mg=24.00$ ,  $Si=28.00$ , and  $Cl=35.00$ . The atomic weights are dependent on that of chlorine, so that an error in chlorine would affect the others in the same way. The probability that this is due to an accident is 1:100,000. The author therefore draws the conclusion that all atomic weights are integers when the standard  $O=16$  is adopted. J. F. S.

**Is the Ratio of the Atomic Weights  $O = 16 : Ag = 107.88$  Correct?** ALOIS BILECKI (*Zeitsch. Anorg. Chem.*, 1919, 108, 113—118).—It has been shown (A., 1917, ii, 197) that the atomic weights of silver, 107.88, bromine, 79.991, and chlorine, 35.46, are multiples of the number  $n_1=0.307350427$ . Thus,  $Ag=351n_1$ ,  $Br=260n_1$ , and  $Cl=115\frac{1}{2}n_1$ . On the other hand, the atomic weights of oxygen and other elements determined with reference to oxygen are multiples of the number  $n=0.307692\frac{1}{2}$  that of oxygen being  $16=52n$ . An examination of the published determinations of the atomic weight of manganese shows that, when this is determined from ratios involving the halogens and silver, for example,  $2Ag:MnBr$ , or  $2AgCl:MnCl$ , the number 54.932 is obtained, which is practically equal to  $178\frac{1}{2}n_1=54.9388$ . When, however, the atomic weight is determined from the analysis of the sulphate, that is, from such ratios as  $MnSO_4:MnO$ ,  $MnO:4O$ , the number 55.0 is obtained, which is equal to  $178\frac{1}{2}n$ . In the case of zinc, also, similar differences are shown between the atomic weights determined with respect to halogens on the one hand and oxygen on the other. It is suggested, on account of these considerations, that, if the atomic weight of silver is taken as 107.88, that of oxygen should not be 16, that is,  $52n$ , but  $52n_1$ , that is, 15.982. In the same way, the atomic weight of sulphur should be 32.026 instead of 32.06. E. H. R.

**The Derivation of Valency Laws. The Principle of Cationic and Partial Valencies.** HUGO KAUFFMANN (*Ber.*, 1919, 52, [B], 1422—1435).—See this vol., i, 50.

**Periodic Precipitates.** The late LORD RAYLEIGH (*Phil. Mag.*, 1919, [vi], 33, 738—740).—Periodic precipitates are best demon-

strated as follows. A glass lantern-slide is carefully cleaned and placed absolutely level. To 5 c.c. of a 10% solution of gelatin, one drop of a concentrated solution of sodium arsenate is added, and poured over the plate while hot. When it is quite set, but before it can dry, a drop of silver nitrate solution containing a trace of nitric acid is allowed to fall on the plate. A series of rings of periodic precipitates of silver arsenate is obtained by this procedure. The greater the concentration of the diffusing solution, the closer the rings are together. The periodicity is supposed to originate from the difficulty of precipitation without a nucleus. One ring having been formed, precipitation occurs thereat until the silver nitrate solution has diffused to a place where a sufficiency of sodium arsenate solution remains to render possible new precipitation. The interval between successive rings increases with increase of distance from the centre of diffusion. Periodic structure is also exhibited when a few drops of a cold saturated solution of copper sulphate and salicin to which is added 3% of strong syrup (sugar) are spread on a microscope slide and warmed, excess of liquid being removed, and the plate kept at about 17° above the ordinary temperature until crystallisation sets in, and then cooled. A polarising microscope reveals a structure periodic some thousand times per centimetre.

J. S. G. T.

**History of the Discovery of the so-called Liebig's Condenser.** R. A. (*Parfumerie Moderne*, 1919, 12, 10—12; from *Chem. Zentr.*, 1919, iii, 209).—The discovery of the counter-current principle in condensers is not attributable to Liebig, but was made independently by a Frenchman, whose name is unknown, in the year 1770, by Christian Weigel in 1771, and by a Finn, Jean Gadolin.

H. W.

**Filter Funnel.** ERICH LEHMANN (*Chem. Zeit.*, 1919, 43, 726).—The stem of the funnel is divided so as to form two narrow channels; the part connecting the upper portion of these two channels forms a support for the point of the filter paper contained in the funnel.

W. P. S.

**Method for Rapid Filtration.** J. DOCTERS VAN LEEUWEN (*Chem. Weekblad*, 1919, 16, 1424—1425).—The author has obtained satisfactory results with the method proposed by Noyes (*Int. Sugar J.*, May, 1919; from *Chem. Anal.*), in which, by tearing off a corner from one or two thicknesses of the folded filter paper, an unbroken stream of liquid is obtained in the stem of the funnel, filtration being thereby accelerated.

W. J. W.

**Tait Vortex-rings and Colloidal Sulphur: with Lecture Experiments.** I. GUARESCHI (*Atti R. Accad. Sci. Torino*, 1917—1918, 53, 321—334). Vortex-rings of mixed air and ammonium chloride vapour are so stable that they are able to traverse successively several layers of water or other liquid, the conclusion drawn by the author being that the ammonium chloride is present



in the colloidal condition. Good rings are also obtainable by forcing sulphur trioxide or phosphoric oxide vapour, by squeezing a rubber bulb, through a U-tube containing water, etc.; the orifice through which the rings issue may be either circular or square. Various procedures are described for obtaining rings by passing the above vapours, mixed with other vapours and gases, through different substances.

When hydrogen sulphide and air are passed together through a U-tube containing either fresh soda-lime or a mixture of quicklime and yellow mercuric oxide, vivid incandescence is observed at a certain point in the U-tube. In the latter case, when the resultant mixture of hydrogen sulphide and sulphur dioxide is passed through water, the latter becomes milky owing to the deposition of colloidal sulphur, which is precipitated in arborescent formation and falls from the surface to the bottom of the liquid in spirals, each of which is terminated by a ring similar to the vortex-rings. A modification of this experiment, for use as a lecture demonstration, is described.

T. H. P.

#### **Soluble Aluminium Phosphate. A Lecture Experiment.**

OLOF SVANBERG (*Zeitsch. anorg. Chem.*, 1919, 108, 70—72).—When to a 1% solution of aluminium chloride, neutralised with ammonia if it has a slight acid reaction, are added a few drops of a 1—2% solution of potassium dihydrogen phosphate, both being coloured yellow by the addition of a drop of methyl-orange solution, the colour of the mixture immediately becomes red without the formation of any precipitate or of any turbidity. When the solution is warmed a precipitate comes down, but there is no further colour change. Measurements were made of the hydrogen-ion concentration in binary solutions of the two salts, and it was found that a maximum occurs with about 40 mols. % of potassium dihydrogen phosphate. Salts of calcium, magnesium, zinc, or cadmium do not give the colour change with the phosphate. Glucinum sulphate does give the reaction, but it is much more sensitive to excess of phosphate.

E. H. R.

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### **Inorganic Chemistry.**

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**Preparation and Testing of Hydrogen of a High Degree of Purity.** JUNIUS DAVID EDWARDS (*J. Ind. Eng. Chem.*, 1919, 11, 961—963).—An apparatus has been devised as a substitute for the Kipp generator. It consists of two connected cylinders, into one of which the zinc is introduced, whilst a tube through a rubber cork in the bottom is connected with the acid flask. The outlet tube has a side connexion, which dips into mercury and serves as a pressure indicator and as a safety valve. Air is exhausted from the cylin-

ders, the acid flask nearly filled with dilute sulphuric acid, and a few fragments of zinc introduced to sweep out the air before the flask is attached to the cylinders. The acid is drawn up into the generator by turning a tap at the top and opening a vent in the stopper of the acid flask. Pure hydrogen is thus at once obtained and fresh acid introduced without admitting air. Tests made in comparison with pure electrolytic hydrogen by means of the interferometer (A., 1915, ii, 478) showed that hydrogen produced by this apparatus contained less than 1 part in 10,000 of impurities. In similar tests of the gas produced by a Kipp generator 83.86% of hydrogen was found to be present seventeen minutes, and 99.97% forty-two minutes after starting. [See also *J. Soc. Chem. Ind.*, 1920, 19A.] C. A. M.

**New Experiment to Demonstrate the Minute Mass of a Hydrogen Atom.** FR. BÜRGI (*Helv. Chim. Acta*, 1919, 2, 703—704).—A yellowish-green fluorescence is distinctly observable in a darkened room when a beam of light is passed through 0.5 c.c. of a solution prepared by dissolving 0.4 mg. of fluorescein in 10 litres of water. The total quantity of hydrogen which can be furnished by the weight of fluorescein present in this solution is  $6 \times 10^{-11}$  grams, which therefore gives an upper limit for the mass of the hydrogen atom. The figure is greatly in excess of the generally accepted value. H. W.

**Composition of the Atmosphere.** AUGUST KROGH (*Math. fysiske Meddelelser*, 1919, 1, No. 12, 1—19).—Our knowledge of the composition of the atmosphere is still quite uncertain, especially in regard to hydrogen and the relation between oxygen and nitrogen. Until very recently little attention has been paid to the variation in the mixture composing the atmosphere at different altitudes. Wegener claims that at a height of 70 km. hydrogen must be the chief constituent of the earth's atmosphere. Benedict has shown by 200 analyses extending over a period of nine months that the percentage of oxygen at the surface or laboratory level never varied more than  $\pm 0.01$  from the average, and that of carbon dioxide never more than  $\pm 0.005$ . The author describes a new gas analysis apparatus with three gas burettes, one for moving the air sample to and from the absorption pipettes, and for saturating the air with moisture, a second convenient in size for measuring the air before and after the absorption of carbon dioxide, and a third which holds the residual gas after the absorption of oxygen. The author discusses general means for reaching more accurate and constant results. The heated platinum wire method has been applied for the detection of combustible gases, and the conclusion is drawn that hydrogen or other combustible gas is present in an amount which is probably less than 0.002%. The percentage of carbon dioxide in the streets of Copenhagen is usually increased by 0.001—0.007. The need of a thorough research to establish the absolute average composition of pure atmospheric air with more certainty, and a study

of its variations, especially in the higher strata of the atmosphere, is strongly urged. Accurate analyses of samples taken simultaneously from aeroplanes at various heights up to 5 or 6 km. would give valuable information in regard to mixing by vertical currents. Automatic sampling by balloons is suggested. Up to the present time the absolute composition of atmospheric air at the earth's surface has been found to be  $\text{CO}_2$ , 0.030%;  $\text{N}_2$ , 79.022%; and  $\text{O}_2$ , 20.948%.

CHEMICAL ABSTRACTS.

**Nitrogen Generator for Laboratory Use.** W. L. BADGER (*J. Ind. Eng. Chem.*, 1919, 11, 1052—1053).—A wide-necked 2-litre bottle is closed with a rubber stopper through which passes one end of a Liebig condenser jacket (without the condenser tube); the lower water-inlet is sealed off, and the upper one is connected with a side-tube which extends through the stopper to the bottom of the bottle. A bulb with delivery tube is sealed on the upper end of the jacket. The bottle is packed with copper wire, and as much ammonia (1:1) saturated with ammonium chloride is poured in as the bottle will hold. The jacket is filled with copper turnings. Air is blown in through a tube reaching nearly to the bottom of the bottle; the oxygen is absorbed rapidly, and practically pure nitrogen escapes from the delivery tube. The passage of the air (or nitrogen) causes the solution to circulate slowly up the jacket and through the side-tube into the bottle again.

W. P. S.

**The Synthesis of Ammonia at Very High Pressures.** GEORGES CLAUDE (*Compt. rend.*, 1919, 169, 1039—1041).—Having previously shown the possibility of using very high pressures for industrial purposes (*ibid.*, 649), the author has studied the synthesis of ammonia at these high pressures, and finds that at a pressure of 1000 kilos./cm.<sup>2</sup> and at a temperature of 536° the yield of ammonia is over 40%. The zone of temperature within which this reaction takes place at a reasonable velocity under such a high pressure is 500—700°.

W. G.

**Behaviour of the Hydronitrogens [Nitrogen Hydrides] and their Derivatives in Liquid Ammonia. VI. Electrolytic Nitridation of Various Anodes in a Solution of Ammonium Trinitride.** A. W. BROWNE, M. E. HOLMES and J. S. KING (*J. Amer. Chem. Soc.*, 1919, 41, 1769—1776. Compare A., 1911, ii, 1084, 1085; 1913, ii, 583).—Solutions of 1 gram of ammonium azide in 36 c.c. of liquid ammonia were electrolysed at -67°, using anodes of copper, silver, cadmium, aluminium, lead, antimony, iron, and nickel. The gas evolved at both anode and cathode was measured, and the loss of weight of the anode determined. It is shown that copper anodes undergo electrolytic corrosion to an extent indicating the formation of some cuprous azide,  $\text{CuN}_3$ , with cupric azide,  $\text{CuN}_4$ , as the main product. No gas was liberated at the anode. With silver, cadmium, lead, and antimony anodes the corrosion resulted in the formation of normal azides,

$\text{AgN}_3$ ,  $\text{CdN}_6$ ,  $\text{PbN}_6$ , and  $\text{SbN}_9$ , without liberation of gas at the anode. Aluminium, iron, and nickel anodes undergo corrosion, accompanied by the liberation of nitrogen. The aluminium anode became coated with a bulky pyrophoric scale of varying colour and texture. Deep red ferric azide,  $\text{FeN}_9$ , was obtained in solution when an iron anode was employed, but this product was ammonolysed and yielded an ammono-basic ferric azide. A pink deposit was formed on the nickel anode, presumably an ammono-basic nickel azide.

J. F. S.

**Some Properties of Nitrogen Trioxide, Pure or in Solution in Nitrogen Peroxide.**

GEORGES BAUME and MARIUS ROBERT (*Compt. rend.*, 1919, 169, 968—970).—The authors have studied the melting-point and vapour-pressure diagrams of the system nitrogen trioxide–nitrogen peroxide. The melting-point diagram is normal, and has a single eutectic in the neighbourhood of the freezing point of pure nitrogen trioxide. From the vapour-pressure curves between  $-80^\circ$  and  $35^\circ$ , the author deduces the b. p. of pure nitrogen trioxide to be  $-27^\circ/760$  mm.

Pure nitrogen trioxide can only exist at very low temperatures in the solid state or in the liquid state under pressure of nitric oxide. At temperatures above  $-100^\circ$  it dissociates. It is not possible to distil it in a vacuum because of the immediate formation of an atmosphere of nitric oxide at temperatures at which distillation is possible.

W. G.

**Silicon Hydrides. VII. Protosiloxane,  $\text{O}:\text{SiH}_3$ .**

ALFRED STOCK and KARL SOMESKI (*Ber.*, 1919, 52, [B], 1851—1860. Compare A., 1918, ii, 111).—In the earlier paper it was shown that dibromomonosilane reacts with water to form polymerides of protosiloxane,  $\text{O}:\text{SiH}_3$ . The unimolecular form has now been obtained as a gas by the action of the required amount of water vapour on dichloromonosilane in a very large flask under greatly reduced pressure. It has an extraordinary tendency to polymerise, much more so than the analogous carbon compound, formaldehyde, in consequence of which the flask must be perfectly clean and smooth. Liquid and solid polymerides are formed immediately on condensation. The liquid ones are like benzene, and can be obtained conveniently as a solution by shaking a benzene solution of dichloromonosilane with water. These benzene solutions are fairly stable towards water, but reduce silver nitrate in the cold. They correspond roughly with  $(\text{SiH}_3\text{O})_n$ . The solid polymerides are insoluble. All the polymerides react with sodium hydroxide according to the equation  $\text{SiH}_3\text{O} + 2\text{NaOH} = \text{Na}_2\text{SiO}_3 + 2\text{H}_2$ .

J. C. W.

**Constitutional Formulæ of Kaolinite and other Silicates.**

RUDOLF WEGSCHEIDER (*Zeitsch. Elektrochem.*, 1919, 25, 352).—It is shown that the constitutional formulæ of polysilicates must be written with the silicon atoms joined through oxygen and not directly with one another. Compounds with the silicon atoms directly united are reducing agents and unstable. Further, if the polysili-

cates are considered as having the silicon atoms directly united it will follow that the oxygen atoms must also be directly united, which again will point to instability. The combination of a strongly reducing group,  $-\text{Si}-\text{Si}-$ , with a strongly oxidising group,  $-\text{O}-\text{O}-$ , will, of necessity, give a compound of an extremely unstable character, which is certainly not the case with the polysilicates. [See also Simmonds, T., 1904, 85, 681; Pukall, A., 1910, ii, 780; Manchot, A., 1910, ii, 1060.] J. F. S.

**Theory of Binary Mixtures. V. Vapour Pressure and Molecular Constitution of Liquid Argon and Argon-Nitrogen Mixtures.** F. DOLEZALEK (*Zeitsch. physikal. Chem.*, 1919, 93, 585—595. Compare A., 1916, ii, 132).—A theoretical paper, in which, using the experimental data previously published, the association constants are calculated from the saturation pressure of the mixture, and also the molecular constitution of the mixtures and pure argon, the saturation pressures of the liquid mixtures and the constitution of the vapour. It is shown that liquid argon is partly composed of diatomic molecules and has an association constant at  $85.11^\circ$  abs. of  $K=0.20$ . Hence at low temperatures argon possesses chemical affinity, and consequently argon compounds are to be expected at low temperatures. There is therefore no fundamental difference between the inactive gases and other gases, but only a difference of degree. When liquid argon is diluted with liquid nitrogen the diatomic molecules dissociate according to the law of mass action. The vapour tension of liquid argon-nitrogen mixtures, as well as the constitution of the vapour, may be calculated at all concentrations by means of the author's theory of solution (A., 1909, ii, 22). J. F. S.

**Preparation of Metallic Potassium.** FRITZ C. WICKEL and WALTER LOEBEL (D.R.-P. 307175; from *Chem. Zentr.*, 1919, iv, 361).—Accurately measured quantities of metallic sodium and potassium hydroxide are melted together with exclusion of air, so that sodium oxide is formed and potassium is volatilised from the mixture (at about  $670^\circ$ ), and suitably condensed. Hydrogen is obtained as by-product. The process is suitable for the manufacturing scale. H. W.

**The Autoxidation of Sodamide.** HANS SCHRADER (*Zeitsch. anorg. Chem.*, 1919, 108, 44—48).—The amides of the alkali metals are known to undergo autoxidation, with the formation of nitrite, hydroxide, and ammonia. When finely divided sodamide is exposed to air in presence of a little water, a yellowish-red oxidation product is formed, which is now shown to be a peroxide, probably of the formula  $\text{NaNH}_2\text{O}_2$ . The peroxide formed was estimated by adding the product to a cold saturated solution of barium chloride, when barium peroxide was precipitated, and was estimated in the usual way. It was found that a sample of sodamide gave in fifty-eight days at ordinary temperature 0.44

mol. % peroxide and 6.9% nitrite. In dry air, autoxidation does not take place at the ordinary temperature, but at 100° to 110° the peroxide is slowly formed. The peroxide is stable in dry air, but in moist air is changed into a white substance, the aqueous solution of which gives the peroxide reaction. E. H. R.

**Solubility and Fusion Relations at High Temperatures and Pressures.** GEORGE W. MOREY (*J. Eng. Club, Philadelphia*, 1919, **35**, 509—519).—An address. The preparation of the compounds *monopotassium aluminat*e,  $K_2O \cdot Al_2O_3$ , large, octahedral crystals, and *monopotassium ferrite*,  $K_2O \cdot Fe_2O_3$ , large, red, octahedral crystals, decomposed by water below 500°, is mentioned.

CHEMICAL ABSTRACTS.

**The Properties of Ammonium Nitrate. I. The Freezing Point and Transition-temperatures.** REGINALD GEORGE EARLY and THOMAS MARTIN LOWRY (*T.*, 1919, **115**, 1387—1404).

**Action of Bromine on Calcium Carbide.** EDWARD BARNES (*Chem. News*, 1919, **119**, 260—261).—Liquid bromine acts slowly on calcium carbide at ordinary temperatures, producing carbon hexabromide and calcium bromide. 4.5 Grams of finely powdered calcium carbide, treated with 45 grams of purified dry bromine in a 50 c.c. bottle for five months, gave a product which, after removal of excess of bromine, weighed 32.4 grams and contained 22 grams of hexabromoethane, 8.8 grams of calcium bromide, and 0.2 gram of unchanged calcium carbide. Calcium carbide and bromine heated in sealed tubes at 100°, until no further action was apparent, produced carbon and calcium bromide. Dry chlorine was found to have no action on calcium carbide exposed to it at the ordinary temperature for two months. S. S. A.

**Reduction of Barium Nitrate by the Alternating Current.** P. WENGER and A. LUBOMIRSKI (*Ann. Chim. anal.*, 1919, [ii], **1**, 339—342).—With lead electrodes, the yield of nitrite increases with the amperage, but with mercury electrodes the maximum yield is obtained with 0.6 ampere; the yield also increases with temperature in the case of lead electrodes, and decreases with aluminium or zinc electrodes. Temperature has little, if any, effect when copper, cadmium, or magnesium electrodes are employed. The oxygen liberated from the nitrate combines with the electrode, forming suboxides (copper, mercury, cadmium, and tin electrodes), hydroxides (lead, zinc, aluminium, and magnesium electrodes), or oxides (nickel and silver electrodes). The nitrate is not reduced by the metallic electrodes unless the current is passing. W. P. S.

**Purification of Magnesia. Conditions in which Periclase or Crystalline Magnesia is Formed.** J. MEUNIER (*Bull. Soc. chim.*, 1919, [iv], **25**, 560—562).—Magnesium oxide may be freed from contained calcium by igniting the material at a red heat and

subsequently, after cooling, extracting it with successive quantities of a 10% sucrose solution until the last extract does not give any turbidity with ammonium oxalate. If such material is then washed with water, dissolved in hydrochloric acid, the solution evaporated to dryness, and the residue gradually heated in a covered crucible until it attains a red heat, magnesium oxide is obtained in the form of crystals of periclase on the lid and sides of the crucible and on the surface of the amorphous oxide in the crucible. The material so obtained is very pure. W. G.

**Concentrated Thallium Amalgams: their Electrochemical and Thermochemical Behaviour; Densities and Freezing Points.** THEODORE W. RICHARDS and FARRINGTON DANIELS (*J. Amer. Chem. Soc.*, 1919, **41**, 1732—1768).—The electromotive force, density, specific volume, specific heat, heat of dilution, and freezing point of thallium amalgams up to a concentration of 40.9% thallium have been experimentally determined. The heat of solution of thallium in mercury and in various amalgams has also been determined. The *E.M.F.* measurements were made at 20°, 30°, and 40°, and are shown to be much greater than demanded by the simple concentration law. The temperature-coefficients of the *E.M.F.*'s have been calculated for the various amalgams, and they are found to be less than is demanded by the gas law and vary as the concentration increases. The solution volume of thallium is remarkably constant, varying only from 17.47 to 17.51, but it is somewhat larger than the specific volume (17.21) of thallium. Thallium, therefore, must expand on amalgamation. The coefficients of expansion were calculated from these results, and found to diminish with increasing concentration. The heat capacities were found to be distinctly larger than the sum of the heat capacities of the thallium and mercury in the amalgam. This excess is greater in dilute than in concentrated amalgams. The heat of dilution with mercury was determined at 20°, and from the results the values at 30° and 325° were calculated. Although the heat of dilution of thallium amalgam is a very different effect from the transfer of thallium from one amalgam to another, it is shown that either of these effects may be calculated from the other. Within the limits of experimental error, the heat effects in the cells of which the *E.M.F.* was measured may be calculated from either the heat of dilution of the amalgams, or the heat of solution of thallium in the amalgams, or the temperature-coefficient of the *E.M.F.*, each of these three methods giving essentially identical results within the limits of experimental error. The freezing points of amalgams containing from 16 to 45 atomic % of thallium were found to give a curve indicating conclusively the existence of the solid compound  $\text{Th}_2\text{Hg}_5$ . The single potential of pure electrolytic thallium was found to be about 2.5 m.v. more negative than that of saturated thallium at the ordinary temperature. J. F. S.

**Nitrous-Nitric Complexes of Thallium.** L. ROLLA and G. BELLADEN (*Gazzetta*, 1919, **49**, ii, 217—224).—Thallium nitrite,

like barium, strontium, and calcium nitrites (compare Vogel, A., 1933, ii, 591), has a specific electrolytic conductivity below that of the corresponding nitrate, and undergoes normal dissociation. The *E.M.F.* of the cell, thallium amalgam|N/10-thallium nitrite|normal electrode, is 0.667 volt at 25°, the same value being obtained if the nitrite is replaced by the nitrate.

Peters found that lead nitrate and nitrite interact in solution, forming well-defined compounds containing both salts. Similarly, thallium nitrite and lead nitrate react, yielding compounds containing Pb, Tl, NO<sub>3</sub>, NO<sub>2</sub>, and OH. With potassium nitrite and thallium nitrate, however, despite wide variations in the concentrations of the reacting solutions, no product containing potassium could be obtained; the nitrate-nitrites formed, although they have compositions differing greatly from those of Peters' salts, are stable and may be recrystallised unchanged. If the two reacting salts are taken in molecular proportions, the resultant product has the percentage composition Tl 76.65, NO<sub>3</sub> 20.58, and NO<sub>2</sub> 2.76, whilst in the proportion TlNO<sub>3</sub> and 2KNO<sub>2</sub> the compound obtained has the formula Tl<sub>2</sub>N<sub>2</sub>O<sub>8</sub>, the ratio of NO<sub>3</sub> to NO<sub>2</sub> in the complex ion being 2:1. With 3 mols. of potassium nitrite and 1 mol. of thallium nitrate, the product has the percentage composition Tl 82.78, NO<sub>3</sub> 6.64, NO<sub>2</sub> 5.80, and OH 4.78, and with 4 mols. of the nitrite to 1 mol. of the nitrate the composition is Tl 86.22, NO<sub>3</sub> 1.27, NO<sub>2</sub> 4.17, and OH 8.34.

T. H. P.

**Investigations on some Rapid Low Temperature Reactions by means of Heating Curves.** J. ARVID HEDVALL and NILS VON ZWEIFBERGK (*Zeitsch. anorg. Chem.*, 1919, **108**, 119—136).—In a previous paper (A., 1919, ii, 26) it was shown that the decomposition of barium peroxide takes place at a much lower temperature in presence of all modifications of silica than when heated alone, a certain amount of barium silicate being formed at the same time. The behaviour of a great number of other oxides when heated with barium peroxide has now been studied by examining the heating curves of the mixtures in molecular proportions. Cuprous oxide reacts violently with barium peroxide at about 130° and is completely oxidised to cupric oxide. The latter decomposes barium peroxide catalytically, the optimum temperature being about 660°. Magnesium and calcium oxides start the decomposition of the peroxide at 250° and 310° respectively, whilst zinc oxide rings about slow decomposition between 200° and 370°, and at the same time forms barium zincate. Purely catalytic action is shown by cadmium oxide, lanthanum oxide, and cerium peroxide, whilst zirconium oxide and stannous and stannic oxide are without action. Alumina acts catalytically and forms an aluminate. Titanium oxide and barium peroxide in molecular proportions, when heated below 300°, evolve oxygen slowly; above 300° a titanate is formed, probably BaTiO<sub>3</sub>. When the proportions 2BaO<sub>2</sub> to TiO<sub>2</sub> are used, a basic titanate, completely soluble in acetic acid, is formed. Litharge and barium peroxide between 300° and 400°



give no oxygen, but form a brown product, the nature of which has not been determined. Above  $500^{\circ}$ , much oxygen is evolved and a product formed, probably  $\text{Ba}_2\text{PbO}_4$ , which leaves a residue of lead peroxide when treated with nitric acid. Vanadium pentoxide reacts vigorously with barium peroxide. When equimolecular proportions are used, reaction begins at  $215^{\circ}$  and is ended at  $530^{\circ}$ , barium metavanadate,  $\text{Ba}(\text{VO}_3)_2$ , being formed. With  $2\text{BaO}_2$ , the metavanadate is first formed, but at  $375^{\circ}$  a second, very vigorous, reaction starts, and the colour changes from brown to white, the product formed being apparently  $\text{Ba}_2\text{V}_2\text{O}_7$ . Tantalum pentoxide also reacts vigorously, with formation of a tantalate. When arsenic trioxide is heated with barium peroxide (3 mols.), arsenic pentoxide is first formed at  $310^{\circ}$  to  $410^{\circ}$ , and above  $465^{\circ}$  evolution of oxygen begins and barium arsenate is formed. Antimony trioxide behaves differently, as at  $200^{\circ}$  oxygen is evolved with almost explosive violence. Bismuth trioxide starts a gradual evolution of oxygen at about  $250^{\circ}$ , and higher oxides of bismuth, or compounds of these with barium oxide, appear to be formed. Chromium sesquioxide is rapidly oxidised above about  $225^{\circ}$  without evolution of oxygen, barium chromate being formed. The oxides  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{U}_3\text{O}_8$ , and  $\text{UO}_3$  all cause evolution of oxygen and form molybdates, tungstates, and uranates respectively. The lower oxides of manganese are all oxidised, barium manganate being formed. Ferric oxide acts catalytically, and at the same time ferrate is formed. Nickel and cobalt oxides both act catalytically, and are at the same time changed into higher oxides, which, however, do not agree in their properties with the known peroxides of these metals.

E. H. R.

**Basic Exchange in Permutite.** V. ROTHMUND and G. KORNFIELD (*Zeitsch. anorg. Chem.*, 1919, **108**, 215—225).—In a previous paper (A., 1918, ii, 315), basic exchange between univalent metals in permutite was studied. The inquiry has now been extended to bivalent metals, with the study of the exchange between copper permutite and the nitrates of magnesium, calcium, strontium, and barium, and it has been confirmed that, with equivalent ions, the reaction is independent of the dilution. The tendency to permutite formation is least with magnesium, and increases steadily from calcium to barium. For the equilibrium between uni- and bi-valent ions, the equation takes the form  $(c_1')^2/c_2' \cdot (c_2/c_1')^2 = K$ , and this formula has been verified for the exchange between silver permutite and barium nitrate, and for that between calcium and sodium in sodium and calcium permutites. In the latter case a gap was found in the series, showing that calcium and sodium permutites are not completely miscible. The equilibrium for these cases is not independent of the dilution. A few experiments on the exchange between lanthanum and silver permutites showed that in this case the dilution has a marked influence on the equilibrium.

E. H. R.

**Preparation of Colloidal Mercury by Cathodic Disintegration.** A. GUTBIER and G. L. WEISE (*Kolloid Zeitsch.*, 1919, **25**, 97—100).—Colloidal solutions of mercury may be prepared by

striking an arc between a clean mercury surface and a thin platinum foil cathode under water. The most suitable current to employ for the purpose is 3–4 amperes at either 110 or 220 volts. By this means, at ordinary temperatures, the sols are obtained, which have a grey colour, and change from light grey to bluish-grey and then to grey as the concentration increases. The sols are not very stable; on keeping, they coagulate in about twenty-four hours, and are coagulated by very small quantities of electrolytes. In all cases, the coagulation is irreversible. Much more stable sols are produced when a protecting colloid is present; thus, using 1:10 or 1:50 gum arabic solution in water, grey sols are produced, which may be preserved for ten to fourteen days. These sols are also very sensitive to electrolytes and are irreversibly coagulated by the addition of alcohol.

J. F. S.

**Scandium.** R. J. MEYER and B. SCHWEIG (*Zeitsch. anorg. Chem.*, 1919, 108, 303–317).—It was shown in a previous paper (A., 1914, ii, 369) that the atomic weight of scandium given in the International tables cannot be accepted as a final figure. The impurities likely to be present in scandium preparations separated by the usual methods from the other rare earths are traces of thorium and of the elements of the yttrium earths. It has now been found that complete separation of scandium from these impurities can be effected by fractional crystallisation of scandium formate or of ammonium scandium fluoride,  $(\text{NH}_4)_3\text{ScF}_6$ . A sample of scandium oxide, the spectrum of which showed no trace of yttrium lines and only faint traces of those of thorium and yttrium, was fractionated by the formate method, and when the most soluble fraction was examined spectroscopically, the lines of all these elements showed up very strongly, showing that the spectroscopic test for them is not so sensitive as is usually supposed. The least soluble fraction appeared to be pure scandium formate, and the atomic weight of the metal, determined by the sulphate method, was 45.33 to 45.35. Ammonium scandium fluoride was crystallised from hot, weakly ammoniacal aqueous solution. The impurities separated first from the hot solution, and after these had been filtered off, the solution was allowed to cool. After two or three such crystallisations, the spectrum of the double salt showed no signs of the presence of foreign elements. Atomic weight determinations on the pure materials thus prepared were made by Hönigschmidt by analysis of scandium bromide, the mean result of a series of experiments pointing to 45.1 as the true atomic weight of scandium (A., 1919, ii, 285–286). This is one whole unit above the accepted value. The present authors confirm Hönigschmidt's conclusion that an exact determination of the atomic weight cannot be made by the sulphate method, on account of the impossibility of preparing a pure scandium sulphate free from both basic and acid salts.

E. H. R.

**The Changes Undergone by certain Alloys of Aluminium.**  
LÉON GUILLET (*Compt. rend.*, 1919, 169, 1042–1043).—It has

been shown previously (A., 1902, ii, 264) that certain alloys of aluminium with either iron, manganese, or nickel rapidly crumble to powder in the air. These experiments have been repeated, and this time the alloys of aluminium with iron or nickel remained stable. The aluminium-manganese alloy, containing 85.4% of manganese, crumbled very rapidly in the air, but more slowly in oxygen, nitrogen, or hydrogen, without gaining in weight. The change is to an allotropic modification. Similarly, an alloy of aluminium and antimony fell to powder in moist air, but not in dry air, but in this case the change was chemical, oxidation taking place.

W. G.

**The Ternary System, Aluminium-Copper-Zinc, with Reference to Zinc in Particular.** V. JAROS (Int. Zeitsch. Metall., 10, 1—44; from Chem. Zentr., 1919, iii, 512—514).

—The literature of the binary systems Al-Zn, Al-Cu, and Cu-Zn is critically reviewed, in addition to that of the ternary system, with reference to copper. The author has chiefly investigated the portion of the system Al-Zn-CuAl-CuZn<sub>4</sub>. This can be resolved into four equilibria triangles, to each of which a ternary, non-variant, pseudo-eutectic point belongs, which (except in one doubtful case) lies outside the equilibrium triangle. At 424°, with 68% zinc, 12% copper, and 20% aluminium, reaction is expressed by the scheme: aluminium mixed crystals + fused mass = Al<sub>2</sub>Zn<sub>3</sub> + CuAl<sub>2</sub>; at 418°, with 72% zinc, 11.5% copper, 16.5% aluminium, the equation is CuAl<sub>2</sub> + fused mass = Al<sub>2</sub>Zn<sub>3</sub> + CuAl; at 406°, with 79.5% zinc, 9% copper, and 11.5% aluminium, equilibrium occurs as follows: Al<sub>2</sub>Zn<sub>3</sub> + CuZn<sub>4</sub> = fused mass; at 385°, with 94% zinc, 1% copper, 5% aluminium, the reaction is CuZn<sub>4</sub> + fused mass = Al<sub>2</sub>Zn<sub>3</sub> + Zn, mixed crystals; at 590°, with 76% zinc, 23% copper, 11% aluminium, equilibrium occurs thus:  $\delta$  + fused mass = CuAl + CuZn<sub>4</sub>. Ternary compounds were not observed. The alloys were prepared by melting the requisite amounts of the pure metals in unglazed crucibles in an electric furnace with alloys containing 20, 50, and 70% of copper. The temperatures were measured with platinum-platinum rhodium or with silver-nickel thermo-elements (calibrated by the m. p.'s bismuth 269°, lead 327°, zinc 419°, 3b 630.5°). The changes in the solid alloy resulting from the decomposition of the compound Al<sub>2</sub>Zn<sub>3</sub> at 256° were not investigated. The microscopic observations were made with sections etched with aqueous sodium hydroxide solution (2%) or alcoholic picric acid (2%).

The mechanical properties of alloys of aluminium, copper, and zinc, rich in the latter, have been investigated; to secure a near approach to the technical alloys, commercial zinc containing about 1% of lead was used. The hardness of slowly cooled specimens in the system Zn-Al increases rapidly with the aluminium content to about 70 at 10% Al, remains constant to about 20% Al, and then increases very slowly; it reaches a maximum in the system Zn-Cu at about 5% Cu, sinks to a minimum at 12—14% Cu, and subsequently increases very rapidly. The minimum of the Zn-Cu alloy

is also observed in the ternary system Al-Cu-Zn in slowly cooled specimens, but is absent from quickly cooled specimens; the hardness increases considerably more uniformly. The tenacity of Cu-Zn alloys shows a maximum at about 10% Cu, whilst that of Zn-Al alloys increases fairly rapidly with addition of copper to about 8-10% Cu, and then sinks. Fractured surfaces of zinc become finer by addition of aluminium without altering the usual structure; addition of copper causes little alteration in the region of the zinc mixed crystals, but subsequently the fracture is more finely granular. The compressibility of alloys of zinc 90%, Cu 6%, and Al 4% has also been investigated. The tenacity and hardness of brass or ordinary bronze is readily attained in Al-Cu-Zn alloys, but the brittleness of the latter make them an imperfect substitute for the former.

The technical possibilities of Al-Cu-Zn alloys rich in the latter are discussed. The maximum useful copper content is estimated at about 10%, the minimum at about 4%. Aluminium should not exceed 5%, and should be diminished with increasing amounts of copper. The alloys are not suitable for steam; they oxidise too readily, only withstand moderate pressure, and are corroded by many salt solutions, alkalis, and natural waters. They can only be used with caution in making parts subject to considerable mechanical strain. They are frequently useful for fine mechanical work, such as physical instruments.

H. W.

**The Ternary Systems,  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  and  $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ .** A. MEISSNER (*Zement*, 8, 296-298, 308-310; from *Chem. Zentr.*, 1919, iii, 511).—The temperature-concentration relationships in the first system of the different crystalline phases in equilibrium with the liquid phases have been investigated, and the results are expressed in diagrams and by a model. A ternary compound,  $2\text{MgO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ , unstable at its m. p. and showing considerable tendency to the formation of mixed crystals, has been observed in two forms; the unstable,  $\mu$ -variety crystallises from glasses at a temperature of about  $950^\circ$ , and passes at a somewhat higher temperature into the stable  $\alpha$ -variety. The properties of both forms, more particularly of the  $\alpha$ -form, are similar to those of the mineral cordierite. The system  $\text{CaO-Al}_2\text{O}_3\text{-MgO}$  is comparatively simple, since it does not yield a ternary compound which is stable in the presence of the liquid phase. Its investigation, therefore, is concerned with the equilibrium of the components  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{MgO}$ , and of their binary compounds,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ ,  $3\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ ,  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ ,  $3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$ ,  $\text{MgO}\cdot\text{Al}_2\text{O}_3$ , in ternary solution. The results are expressed in a series of temperature-concentration diagrams. A new form of aluminium oxide is designated  $\beta\text{-Al}_2\text{O}_3$ . The relationship of each of the forms in the binary system  $\text{MgO-Al}_2\text{O}_3$  demands the presence of solid solutions, the amount of which has been estimated.

H. W.

**Manganese-Bismuth, Manganese-Zinc, and Manganese-Silver Alloys.** PAUL SIEBE (*Zeitsch. anorg. Chem.*, 1919, 108, 161-183).—The condition diagram for manganese-bismuth alloys

has been determined by the cooling curve method. The two metals are not completely miscible. When more than 23% of manganese is present, two layers are formed, the upper consisting of practically pure manganese, whilst the lower is a 23% solution of manganese in bismuth. Five arrest points were found, corresponding with five crystalline phases. The eutectic horizontal is at  $259^{\circ}$ , and the other four horizontals, corresponding with the arrest points, are at  $442^{\circ}$ ,  $597^{\circ}$ ,  $1043^{\circ}$ , and  $1252^{\circ}$ . The last represents a eutectic containing at most 0.5% bismuth, which lowers the melting point of manganese  $13^{\circ}$ . From alloys containing up to 0.5% of manganese, pure bismuth first separates; with 0.5 to 9% of manganese, the first compound separates; from 9% to 11% a second compound, and from 11% to 20% a third. The nature of the compounds has not been determined. Between 23% and 99.5% of manganese there is a complete gap. The microscopic appearance of the different crystalline phases is described. The hardness of the alloys increases with the manganese content. They are ferromagnetic, and this property has been shown to be peculiar to the first compound, crystallising from alloys containing between 0.5% and 9% of manganese.

Alloys of zinc and manganese could be prepared containing only up to 50% of manganese. Those containing from 0% to 11% of manganese show an arrest point at  $416^{\circ}$ , the eutectic point. The eutectic compound contains a very small, undetermined quantity of manganese, which lowers the melting point of zinc  $3^{\circ}$ . The mixed crystal constituent of the eutectic contains 11% of manganese, and a series of mixed crystals are formed containing up to 50% of manganese. The alloys are brittle and increase in hardness as the manganese content increases.

The behaviour of a series of manganese-silver alloys with a number of chemical reagents has been studied. A sharp distinction was found between those containing 0.22 and 0.24 mol. of manganese and those containing 0.26 and 0.28 mol. respectively. The latter pair were readily attacked by silver sulphate solution, with deposition of silver; by copper acetate and copper sulphate, with deposition of copper; and by sulphuric and hydrochloric acids, with liberation of hydrogen, whilst the former pair, containing less manganese, were unattacked. There was found a similar sharp difference when the electric potentials of the two pairs were compared. Those alloys containing more than 0.25 mol. of manganese appear to behave, both chemically and electrically, practically as pure manganese.

E. H. R.

**Fluoro-salts of Tervalent Manganese.** I. BELLUCCI (*Gazzetta*, 1919, 49, ii, 180-186).—The author has isolated the trivalent manganese fluoro-salt which causes the anomalous results obtained when Lunge's method of estimating nitrous acid by means of permanganate is applied to solutions containing fluorine ions in high concentration (compare A., 1919, ii, 476). This salt,  $K_2MnF_6 \cdot 11H_2O$ , which belongs to the only known type of fluo-salts of trivalent manganese, may be obtained by the action of nitrous acid in

presence of hydrofluoric acid either on potassium permanganate or on a manganous salt, the nitrous acid acting in the former case as a reducing agent and in the latter as an oxidising agent.

T. H. P.

**The Atomic Weight of Iron.** ALOIS BILECKI (*Zeitsch. anorg. Chem.*, 1919, 108, 318—320).—In a previous paper, the atomic weights of silver and oxygen were compared through that of manganese (this vol., ii, 26). A similar comparison can be made through the atomic weight of iron. Baxter, by analysis of ferrous bromide, found  $\text{Fe}=55.8378$  when  $\text{Ag}=107.88$ , or  $\text{Fe}=55.90$  when  $\text{Ag}=108.00$ . By analysis of ferric oxide, Richards and Baxter obtained in two series of experiments 55.90 and 55.883, taking  $\text{O}=16$ . A careful comparison of the data of the individual experiments establishes the fact that the ratio of silver to oxygen must be 108:16 or 107.88:15.9822, thus confirming the conclusion which was arrived at from a consideration of the atomic weight of manganese.

E. H. R.

**The Penetration of Iron by Hydrogen.** T. S. FULLER (*Trans. Amer. Electrochem. Soc.*, 36, 16 pp.).—Penetration of iron by molecular hydrogen begins at  $325^{\circ}$  and increases rapidly with the temperature, but nascent or atomic hydrogen penetrates iron at the ordinary temperature, as shown by these experiments. An iron tube with 1/16-in. walls, connected at the top to a U-tube device for measuring the volume of gas entering the tube through its walls, was immersed in a 1% solution of sulphuric acid. Hydrogen generated on the outside of the tube passed through the walls, the rate varying with the conditions. The rate was greater for a unit immersed without electrical connections than when the unit was used as a cathode, but in the latter case the greater the current the greater is the penetration. The rate also increases with temperature. Copper is not penetrated by nascent hydrogen, but a coating of tin on the iron increases the rate. Results are given for other conditions and electrolytes. It was proved that there was no penetration by acid, but by gas alone.

CHEMICAL ABSTRACTS.

**Tin Hydride. I.** FRITZ PANETH and KARL FÜRTH (*Ber.*, 1919, 52, [B], 2020—2029).—The authors have applied the method which was successfully used in the study of bismuth hydride (Paneth and Winternitz, A., 1919, ii, 68) to the problem of the isolation of a hydride of tin. An alloy of tin and magnesium, corresponding with the formula  $\text{Mg}_3\text{Sn}$ , is dissolved in 4N-hydrochloric or sulphuric acid; the gas which is evolved is filtered through cotton-wool, dried by calcium chloride and phosphoric anhydride, and led through a heated hard-glass tube; a mirror of metallic tin is formed in close proximity to the hot part of the tube, which, when well developed, consists of three zones, a whitish-grey, blackish-grey to black, and finally brown in colour. The reactions of the mirror

are very fully described, the most distinctive of them being the insolubility in cold, concentrated nitric acid, and the formation of purple of Cassius and calomel by gold and mercuric chlorides, respectively, after preliminary treatment of the ring with dry, gaseous hydrogen chloride. Preliminary experiments also show that the gas can be condensed by liquid air and re-evaporated without decomposition, so that its collection in some quantity appears possible. The yields, however, are as poor as in the case of bismuth hydride, only a few thousandths per cent. of the tin of the alloy being converted into the hydride.

[With A. MARSHALL.] Preliminary experiment appears to show that lead hydride can exist in the gaseous state. It is formed from the magnesium-lead alloy in yield which is worse than in the cases of bismuth or tin, but better results are obtained by an electrolytic process of reduction.

H. W.

### The Question of the Existence of Zirconium Monoxide.

ROBERT SCHWARZ and HUGO DEISLER (*Ber.*, 1919, 52, [B], 1896—1903). Winkler (A., 1890, 1375), Dennis and Spencer (A., 1896, ii, 558), and Wedekind (A., 1905, ii, 596) have studied the reduction of zirconium dioxide by magnesium, and obtained black powders which recombined with oxygen on heating in the air, the increase in weight approximating to that required by the formula  $\text{ZrO}$ . The experiments have been repeated under various conditions (in a Rose crucible, in a combustion tube in an atmosphere of carbon dioxide, in porcelain tubes at  $1000^{\circ}$  filled with carbon dioxide or hydrogen or evacuated, and in a crucible fired by thermite), but it is found that it is quite accidental that the black powder left after removing the excess of magnesium and its oxide should increase by the theoretical quantity (nearly 15%) on heating in oxygen. In fact, the more quickly the reduction is performed, the greater is this subsequent absorption of oxygen, rising in one case to 28%.

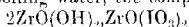
It appears, therefore, that the black powder is a mixture of metallic zirconium and its dioxide. To test this assumption, various specimens of the powder were heated at about  $250^{\circ}$  in a stream of chlorine or at high temperatures in hydrogen chloride gas, the sublimate being analysed. It was expected that the free metal would give the tetrachloride, the dioxide remain unattacked, and the monoxide, if any, produce water in the case of hydrogen chloride. No indication whatever could be obtained of the presence of the monoxide. The sublimate consisted of the tetrachloride and its weight agreed exactly with the increase of weight suffered by the powder when heated in oxygen. The dioxide is not attacked at all, even at  $500^{\circ}$ .

J. C. W.

### Zirconyl Compounds with the Oxy-halogen Acids. F. P.

VENABLE and I. W. SMITHEY (*J. Amer. Chem. Soc.*, 1919, 41, 1722—1727). Zirconium hydroxide does not dissolve in iodic acid, and therefore zirconium iodate was prepared by adding iodic acid solution to a solution of zirconyl chloride, when a white precipitate,

insoluble in water, alcohol, and ether, was obtained. It was decomposed by hydrochloric acid, with evolution of chlorine, and at  $125^{\circ}$  iodine was evolved. The precipitate was filtered without any washing, and other samples were filtered and washed with measured volumes of water with the object of determining the amount of hydrolysis. The unwashed precipitate had the composition  $\text{ZrO}(\text{OH})_2 \cdot 2\text{ZrO}(\text{IO}_3)_2$  when obtained from concentrated solutions, but from dilute solutions the salt is more basic and has the composition  $5\text{ZrO}(\text{OH})_2 \cdot 8\text{ZrO}(\text{IO}_3)_2$ . When the second compound was washed with 6 litres of water at the ordinary temperature, the compound had the composition  $3\text{ZrO}(\text{OH})_2 \cdot 4\text{ZrO}(\text{IO}_3)_2$ . On washing with 20 litres of boiling water, the compound



was obtained, and with 30 litres of boiling water the compound  $3\text{ZrO}(\text{OH})_2 \cdot \text{ZrO}(\text{IO}_3)_2$  was produced. Zirconium hydroxide is readily soluble in 30% perchloric acid. When the action was allowed to take place at the ordinary temperatures, the compound  $\text{ZrO}(\text{ClO}_4)_2 \cdot \text{HClO}_4$  crystallised out in large, triclinic crystals, but when perchloric acid was heated with an excess of zirconium hydroxide, the compound  $\text{ZrO}(\text{OH})_2 \cdot 9\text{ZrO}(\text{ClO}_4)_2$  was obtained in crystal clusters, which were soluble in alcohol, ether, benzene, chloroform, or carbon tetrachloride, but could not be recrystallised from these solvents. On adding potassium chlorate to a cold concentrated solution of zirconyl perchlorate, crystals of basic zirconyl chlorate,  $\text{ZrO}(\text{OH})_2 \cdot 3\text{ZrO}(\text{ClO}_3)_2$ , were obtained. The crystals were extremely deliquescent, very soluble in alcohol, but insoluble in ether. They were faintly yellow in colour, had an odour of chlorine dioxide, and oxidised organic matter very readily.

J. F. S.

#### Elimination of Vanadium from the Arsenical Waters of the Bellville District, Province of Córdoba, Argentine.

FREDERICO REICHERT and RAUL WERNICKE (*Anal. Soc. Quim. Argentina*, 1919, **7**, 110-113). Solutions of ferric salts and of ferrous sulphate added in small quantities to alkaline solutions of sodium vanadate cause the precipitation of the vanadium as insoluble ferric vanadate, and also by adsorption on the ferric hydroxide formed. It is proposed to apply the method for the simultaneous removal of arsenic and vanadium from natural waters.

W. S. M.

#### [Preparation of Potassium Pyroantimonate for the Estimation of Sodium.]

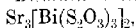
J. D. VAN LEEUWEN (*Chem. Weekblad*, 1919, **16**, 1426).—Potassium pyroantimonate, which will remain unaffected for a prolonged period, is made as follows: 20 grams of potassium antimonyl tartrate are mixed with an equal quantity of potassium nitrate, and the mixture is heated to redness in a crucible. When reaction has ceased, the lid is placed on the crucible, and heating continued for fifteen minutes. After cooling, 50 c.c. of warm water are added, and the mass stirred until it



becomes powdery. It is then filtered through a porcelain vacuum filter, the residue is treated with 100 c.c. of cold water, and transferred with the filter paper to a flask containing 500 c.c. of boiling water. After boiling for one minute and rapidly cooling, some aluminium hydroxide is added, the mixture is shaken, and finally passed through an ordinary filter paper.

W. J. W.

**Bismuth Thiosulphate Compounds.** L. VANINO and F. MUSSGANG (*Arch. Pharm.*, 1919, **257**, 264—266).—The authors have prepared various double thiosulphates of bismuth by making use of bismuth-mannitol solution. Hauser (A., 1903, ii, 487) describes an unstable bismuth sodium thiosulphate, but a stable compound,  $\text{BiNa}_2(\text{S}_2\text{O}_3)_3$ , which crystallises in small octahedra, is obtainable by the interaction of bismuth-mannitol solution and sodium thiosulphate in presence of manganese chloride. *Bismuth ammonium thiosulphate*,  $\text{Bi}(\text{NH}_4)_3(\text{S}_2\text{O}_3)_3 \cdot 2\text{H}_2\text{O}$ , forms a yellow precipitate, which soon changes colour, and on solution in water undergoes decomposition. *Bismuth strontium thiosulphate*,



prepared from bismuth-mannitol solution and strontium thiosulphate, forms a yellow, indistinctly crystalline mass, and undergoes hydrolysis when dissolved in water. The bismuth-silver compound, similarly obtained, forms a yellow precipitate, becoming black in a few seconds; the bismuth-copper compound is precipitated only on addition of alcohol.

Unsuccessful attempts were made to prepare bismuth dithionate and trithionate. On addition of sodium trithionate (compare Willstätter, A., 1903, ii, 543) to bismuth-mannitol solution, the liquid soon blackens; as this behaviour is not shown by sodium dithionate, the presence of bivalent sulphur in trithionic acid is proved.

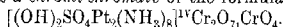
T. H. P.

**Platotriammine Sulphite.** D. STRÖMHOLM (*Zeitsch. anorg. Chem.*, 1919, **108**, 211—214).—When the ammonium salt of trichloroplatosulphonic acid is warmed in aqueous solution with excess of ammonia, *platotriammine sulphite*,  $\text{Pt}(\text{NH}_3)_3\text{SO}_3$ , is formed as a sparingly soluble, white, microcrystalline powder. It seems to be identical with the substance which was described by Birnbaum (*Annalen*, 1869, **76**, 142) as platotetrammine sulphite. When its hydrochloric acid solution is oxidised with chromic acid, the diammine,  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ , is formed. Solubility determinations showed that only the *trans*-isomeride was formed. This conclusion was confirmed by the preparation of the oxalate, which is quite distinct from that given by the *cis*-compound.

E. H. R.

**Platinitetrammine Disulphite.** D. STRÖMHOLM (*Zeitsch. anorg. Chem.*, 1919, **108**, 184—190).—To determine definitely whether the compound prepared by Cleve by the action of sulphurous acid on Gros's nitrate,  $\text{PtCl}_2(\text{NH}_3)_4(\text{NO}_3)_2$ , contains bi- or quadri-valent platinum, a study of its formation, reduction,

and oxidation has been made, with the result that the compound has been proved to have the composition  $\text{Pt}(\text{NH}_3)_4(\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$ . The yield of the disulphite obtained from the nitrate is only about 66% of the theoretical, and a certain amount of sulphuric acid is formed during the reaction, but not so much as would be required to be formed if the platinum were reduced from the quadrivalent to the bivalent condition. When the compound is oxidised by means of chromic acid, the oxygen used is all accounted for by the oxidation of the sulphurous acid to sulphuric acid, that is to say, there is no oxidation of the platinum. The product of the chromic acid oxidation is a *chromi-chromate* of the formula



By prolonged heating with dilute sulphuric acid, this compound is transformed into the salt,  $[(\text{OH})(\text{SO}_4)\text{Pt}(\text{NH}_3)_4]\text{Cr}_2\text{O}_7$ , previously prepared by Cleve. The same two chromates were prepared from Rajewski's nitrate,  $[(\text{OH})\text{ClPt}(\text{NH}_3)_4](\text{NO}_3)_2$ .

When the platinitetrammine disulphite is boiled with water or heated with acids, platinitetrammine sulphate is formed, the quadrivalent platinum being reduced by half the sulphurous acid, which becomes oxidised to sulphuric acid, whilst the other half of the sulphurous acid escapes. The same reaction takes place incompletely when the salt itself is heated.

E. H. R.

## Mineralogical Chemistry.

**The Genesis of Petroleum as Revealed by its Nitrogen Constituents.** CHARLES F. MABERY (*J. Amer. Chem. Soc.*, 1919, 41, 1690—1697).—It has already been shown that the heavier varieties of petroleum in the California, Texas, Ohio, Canada, Russian, and similar fields are complex mixtures of the denser hydrocarbons with oxygen, sulphur, and nitrogen derivatives. They all differ widely in composition from the lighter varieties in the eastern territory. An examination of twenty-one specimens of the latter, however, discloses in every case the presence of nitrogen in amount varying from 0.01 to 0.48%, so that the conclusion is justified that nitrogen is contained in the petroleum of all the principal oil fields in forms of combination which could have had their origin only in the remains of vegetable or animal bodies. Presumptive evidence has been shown that the associated hydrocarbons in petroleum had the same origin.

Nitrogen is estimated by Kjeldahl's method on the one hand and by a process which is a combination of the Dumas procedure for nitrogen and the oxygen combustion for carbon on the other. For details of the latter and of the special precautions required in the estimation of such minute proportions of nitrogen in oils, the

original paper must be consulted. The results obtained by the two methods show very fair agreement. H. W.

**Probable Identity of Peganite with Variscite.** LORENZO MOSCHETTI (*Atti R. Accad. Sci. Torino*, 1917—1918, **53**, 652—656).—The author has analysed and examined physically Breithaupt's peganite (*J. Chem. Physik*, 1830, **60**, 308), his results indicating the identity of this mineral with variscite. The composition given by Hermann (*J. pr. Chem.*, 1844, **33**, 287) for peganite is erroneous. T. H. P.

**Identity of Spangite with Phillipsite.** F. ZAMBONINI (*Atti R. Accad. Sci. Torino*, 1917—1918, **53**, 47—54).—The spangite described by Mantovani (private communication, 1872) is found to be devoid of magnesium, and its crystallographic characters show that it is identical with the phillipsite of the leucitites found in the neighbourhood of Rome. T. H. P.

**The Minerals of the Valley of Gava in the Voltri Group; a New Variety of Talc.** EMILIO REPOSSI (*Atti Soc. Ital. Sci. Nat.*, 1918, **57**, 131—155). The geology of the region is outlined and a number of minerals described. Crystallography or other features are given of garnet, vesuvianite, diopside, hornblende, chlorite, titanite, apatite, pyrite, magnetite, ilmenite, and calcite. Many of these are coated with a mineral, which seems to be a new variety of talc, and is named *garite*, after the locality. Its properties are: colour, milk-white, yellow, or green, sometimes the colour of nickel salts; lustre in mass, velvety, on surfaces of individual blades, pearly; structure, thin crusts with mammillary surface, made up of bunches of flakes. Microscopic study shows aggregate polarisation, with the optical properties: elongation, +; extinction, parallel; interference colours, brilliant;  $n$  1.541 and 1.582 by immersion method, about, double refraction thus 0.038; in all these properties it is similar to talc. It is infusible before the blowpipe, responds to tests for magnesium and silica, and is somewhat readily soluble in hydrochloric acid. Analysis gave:

SiO <sub>2</sub> .	MgO.	Fe <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O at 110°.	H <sub>2</sub> O above 110°	Total.
59.20	28.57	3.23	1.45	6.61	99.06

The water is expelled in two definite stages, in the amounts stated. Disregarding the water below 110°, the revised percentages correspond with the formula  $H_4(Mg,Fe)_3Si_4O_{12}$ . *Garite* differs from talc in the high content of water and in its solubility in acid.

CHEMICAL ABSTRACTS.

**The Oxidation of Lava by Steam.** J. B. FERGUSON (*J. Washington Acad. Sci.*, 1919, **9**, 539—546). It is generally supposed that water vapour in volcanic gases would have an oxidising action on any ferrous iron present in the lava. Fresh Kilauean lava has been shown to contain 9.28% ferrous oxide and 1.92% ferric

oxide, and this fact might be used as an argument against the presence of a preponderance of water vapour in the gases. Very little is known, however, of the action of steam on silicate minerals containing ferrous iron, and a number of experiments are here recorded in which ground Kilauean lava was exposed to the action of water vapour in an atmosphere of nitrogen at 1000°. As a result of the heating, there was found a slight decrease in the ferrous iron content of the rock, but this occurred both in presence and absence of steam, which behaved as an inert gas. The experiments leave no doubt that a considerable amount of ferrous iron, when in silicate combinations, can exist in the presence of water vapour at high temperatures. When a sample of the lava was heated strongly in air for two hours, the ferrous iron content fell to 1.94%, but on again heating in a partial vacuum for four hours at 1100°, it rose again to 3.9%. The bearing of these experiments on the interpretation of results obtained by pumping gases from rocks at high temperatures is emphasised.

E. H. R.

**Cumberland Falls Meteorite.** ARTHUR M. MILLER (*Science*, 1919, **49**, 541--542).—This meteorite was seen at midday on April 9th, 1919, passing over north-eastern Tennessee in a course N. 30 W., its progress being noted and in some instances timed by telegraph and telephone operators. It reached the earth in south-eastern Kentucky, striking with earthquake violence. At the time of writing, seven pieces, ranging from 360 to 2378 grams, have been found, and their covering of glaze indicates that the splitting off from the main mass occurred at a considerable distance from the ground. Fifty-two pieces, weighing from less than 20 grams up to 1800 grams, have been found that are parts of a mass weighing originally about 14 kilos. A chemical examination by ALFRED PETER shows the mineral to be mainly enstatite, through which is disseminated particles of nickel-iron and iron sulphides. D 318.

CHEMICAL ABSTRACTS.

### Analytical Chemistry.

**The Process of Preparation of Charcoal Sticks for Reduction.** NESTOR C. ALEXANDRESCU (*Bull. Soc. chim. Roumanie*, 1919, **1**, 11-12). The following process for the preparation of charcoal sticks for the reduction test in qualitative analysis is advocated. Thin wood chips, such as are used in match making, are boiled for two minutes in a 2.5% solution of ammonium phosphate, and then dried at a temperature not exceeding 60°. When it is required to carry out the test, half the stick is burnt, and then the test is carried out in the usual manner on the substance previously mixed with sodium carbonate.

W. G.

**Titration with Surface-active Substances as Indicators. Estimations of Acidity with the Homologues of the Fatty Acids Series.** WILHELM WINDISCH and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1919, **97**, 135—156).—Adopting Traube and Somogyi's method (A., 1915, ii, 101) of estimating the reaction by means of the alteration in the surface tension brought about by the displacement of the acid or the base of the indicator by the acid or base of the medium, the authors tried the homologues of the salts of the fatty acids series up to undecylic acid as indicators. The acids with  $C_9$ – $C_{11}$  have been found to be as sensitive as litmus and neutral-red. Free acids can be estimated in the presence of a primary phosphate by using the above acids as indicators.

S. S. Z.

**A Considerable Source of Error in Titrations in the Presence of Phenolphthalein.** HAUSERMANN (*Süddentech. Apoth. Zeit.*, 1919, **59**, 361—362; from *Chem. Zentr.*, 1919, iv, 396).—The author directs attention to the errors, caused by the presence of free carbon dioxide in distilled water, which occur in titrations in which phenolphthalein is used as indicator. H. W.

**Preparation of Phenolphthalein Solution and Paper without the Use of Alcohol.** H. CLAASSEN (*Zentr. Zuckerind.*, **26**, 209; *Arch. Suikerind.*, 1919, **26**, 1588—1590).—When alcohol is unavailable, an indicator solution may be prepared by dissolving 1 gram of phenolphthalein in 12.5 c.c. of *N*-sodium hydroxide, and diluting to 500 c.c. with water. The alkali content of the solution is so small that it can be disregarded in factory work. Where greater accuracy is required, the result can be corrected for the alkalinity of the indicator. Test paper can be prepared by immersing paper first in a solution made by diluting 200 c.c. of the above indicator solution to 1 litre, drying, immersing it in a solution of sulphuric acid of the proper strength to give the desired acidity, and drying again. The results obtained with the paper should be verified from time to time by direct titration.

CHEMICAL ABSTRACTS.

**Estimation of Bromine in Mineral Waters and Brines.** W. F. BAUGHMAN and W. W. SKINNER (*J. Ind. Eng. Chem.*, 1919, **11**, 954—959).—Chromic acid liberates bromine from bromides quantitatively at the ordinary temperature, and the bromine may be removed by aspiration. Chlorides under the same conditions yield only a trace of chlorine, which probably forms chromyl chloride and remains in solution. When a mixture of chlorides and bromides is treated with the reagent, some chlorobromide is formed, and is removed, together with the bromine, on aspiration. In the method of analysis described, the residue from the mineral water is oxidised with chromic acid, with the addition of hydrogen peroxide, and the liberated halogens absorbed in a solution of sodium sulphite and carbonate. This is evaporated, and the residue

again oxidised with chromic acid, and a current of air aspirated through the apparatus, the absorption vessels of which contain potassium iodide solution. In this second aspiration the quantity of chlorine present is so small that only pure bromine is evolved, and its amount is found by titration of the liberated iodine. [See also *J. Soc. Chem. Ind.*, 1920, 19A.] C. A. M.

**Test Paper for the Detection of Iodine.** ANONYMOUS (*J. Pharm. Belg.*, 1919; from *Ann. Chim. anal.*, 1919, [ii], 1, 357).—One gram of starch is mixed with 10 c.c. of water, 40 c.c. of boiling water are added, the mixture is boiled for two minutes, and 0.5 gram of sodium nitrite is then added. The paste obtained is painted on strips of paper by means of a brush, and the strips are dried. To make the test, a few drops of the solution under examination are poured on the paper, followed by one drop of dilute sulphuric acid. A blue coloration is obtained if the solution contains iodide. The test paper keeps well. W. P. S.

**The Spectrocomparator, an Apparatus for the Estimation of the Percentage Saturation of Blood with Oxygen or Carbon Monoxide.** AUGUST KROGH (*J. Physiol.*, 1919, 52, 281—287; from *Chem. Zentr.*, 1919, iv, 210—211).—A modification of Hartridge's method (*A.*, 1912, ii, 488) is proposed which gives satisfactory results and only requires small amounts of blood. The apparatus is fully described and figured in the original, which must be consulted for details. H. W.

**Method for bringing Elementary Sulphur into Solution for Analysis.** A. P. BJERREGAARD (*J. Ind. Eng. Chem.*, 1919, 11, 1055).—The finely divided sulphur is dissolved in a small quantity of dry bromine, nitric acid is added, and the mixture heated. The oxidation requires a few minutes only; after the excess of bromine has been expelled, the mixture is diluted with water, boiled with the addition of hydrochloric acid to expel nitric acid, and the sulphuric acid is then precipitated in the usual way as barium sulphate. W. P. S.

**Non-protein Sulphur of the Blood.** M. KAHN (*Proc. Soc. Exp. Biol. Med.*, 1919, 16, 139; from *Physiol. Abstr.*, 1919, 4, 374).—A method of fractionating and estimating the non-protein sulphur of the blood is described. J. C. D.

**The Titration of Sodium Thiosulphate Solutions.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, 56, 644—657).—The preparation, testing, and application of various substances for the standardisation of thiosulphate solutions are described in detail, and their relative merits for the purpose discussed. The purest forms of potassium dichromate obtainable commercially contain free chromic acid or potassium chromate. A method for the detection and estimation of these is given which depends on the location of a discontinuity in the conductivity curve on the addition of alkali or acid.

If chromic acid is present the addition of standard alkali causes no increase in the conductivity of a dichromate solution until the free acid is neutralised. Similarly, no increase in conductivity is observed on the addition of acid to a solution containing chromate until all the latter has been converted into dichromate. For analytical purposes it is recommended to melt the pure dichromate in an electric furnace before use. The other substances examined are iodine, oxalic acid, cyanogen iodide, potassium iodate, and potassium bromate. All these are easily purified, and give results in the titration of thiosulphate with an error of less than 0.1%. The greatest error, 0.07%, was observed in titrating with dichromate.

W. S. M.

**Influence of the Position of Substituents on the Behaviour of Aromatic Nitro-compounds in the Kjeldahl Estimation of Nitrogen.** B. M. MARGOSCHES and ERWIN VOGEL (*Ber.*, 1919, 52, [B], 1992--1998).—The behaviour of the isomeric nitrophenols, nitrobenzoic acids, and nitrobenzaldehydes when treated with sulphuric acid and potassium sulphate has been investigated; it is found that the nitrogen content of the ortho-derivatives can be correctly estimated in this manner, but that the results for the meta- and para-derivatives are much too low. The favourable action of the hydroxy- or alkyloxy-group in the ortho-position to the nitro-group is further shown by the fact that the process gives exact results with 2-nitroresorcinol, 3-nitro-*p*-cresol, and *o*-nitrophenetole, but low results with *p*-nitrophenetole. A further series of experiments shows that the presence of *o*-nitrophenol or of *o*-nitrobenzoic acid has a favourable influence on the behaviour of the corresponding meta- and para-derivatives, and that this action cannot be ascribed solely to their content of phenol or benzoic acid. The possibility that condensation products of the *o*-nitro-compounds may be the active agents has led to an investigation of the behaviour of phthalic acid, phthalic anhydride, and phenolphthalein under like conditions, but the expected favourable action was not observed. The use of salicylic acid appears particularly advantageous in the case of meta-compounds. It is somewhat remarkable that the three isomeric nitrocinnamic acids yield accurate results.

A further series of determinations is recorded with 2:4-dinitrophenol, 2:4-dinitro-*α*-naphthol, 2:4-dinitrobenzoic acid, 2:4-dinitrotoluene, 3:5-dinitrobenzoic acid, 2:6-dinitrotoluene, and 2:4:6-trinitrophenol; the results are considerably too low in every case, although concordant among themselves. The facts, however, that the 2:4-dinitro-compounds give higher values than the corresponding 3:5- or 2:6-dinitro-derivatives, and that 2:4-dinitrophenol gives results almost identical with those obtained with 2:4-dinitrotoluene, are in accordance with the observations made with the mononitro compounds.

H. W.

**Grete's Volumetric Method (for Estimating Phosphoric Acid).** R. W. TUINZING (*Landw. Versuchs.-stat.*, 1919, 94, 191--195. Compare A., 1916, ii, 490).—This method was found

to be trustworthy. Directions are given for the preparation of the ammonium molybdate-gelatin solution used, and for the recovery of ammonium molybdate from the residual solutions. W. P. S.

**Behaviour of certain Organic Arsenic Compounds in Marsh's Test.** DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1919, 58, 385--390).—The addition of platinum chloride to promote the evolution of hydrogen is inadvisable, even in the case of mineral arsenic, since it may fix part of the arsenic as platinum arsenide. In the case of cacodylic acid, platinum chloride in large excess combines to form a double compound, cacodylplatinochloride, which may remain undecomposed. An analogous compound is formed between platinum chloride and methylarsinic acid. Cacodylic acid, in Marsh's test, produces an orange-yellow deposit in addition to the ordinary black deposit. This probably consists of erythrarsine. By heating the hydrogen flask to about 335° in a bath of melted lead only the orange-yellow deposit is obtained. Methylarsinic acid and neosalvarsan under the same conditions also yield yellow deposits, but these may be distinguished from the cacodylic acid deposit by the fact that during the formation of the former the gas does not form dense, white fumes. The gas from the methylarsinic acid test gives a yellow precipitate with Bettendorf's reagent (stannous chloride solution saturated with hydrogen chloride), whilst the lemon-yellow ring from neosalvarsan is only formed at a high temperature, does not change to black, and is readily soluble in ammonia solution. Atoxyl and salvarsan yield only the ordinary black rings in the test. [See also *J. Soc. Chem. Ind.*, 1920, 42A.]

C. A. M.

**Separations in the Arsenic Group.** WILHELM STRECKER and ADOLF RIEDEMANN (*Ber.*, 1919, 52, [B], 1935-1947).—The authors recommend the following modification of the distillation method for the estimation of arsenic. The arsenic solution is placed in a flask provided with a dropping funnel and connected through an efficient worm condenser with a vessel containing water; the flask is half filled with concentrated hydrochloric acid, potassium bromide (1.5 grams), and a few pieces of porous earthenware are added. The contents of the flask are heated to gentle boiling, and thionyl chloride (10 c.c.) is gradually run in at such a rate that the time of addition is half an hour. The distillate is diluted with water to 700-800 c.c., boiled under reflux in a brisk current of carbon dioxide until sulphur dioxide is completely expelled, and the sulphur has collected (this should be the case in half an hour at the most), and filtered. Arsenic is estimated in the filtrate as the trisulphide. Phosphorus trichloride (25 c.c.) may replace the thionyl chloride, in which case the subsequent boiling of the distillate is unnecessary; on the other hand, the presence of phosphorous acid in the residue often causes complications in subsequent estimations. The method gives accurate results, and can be applied to the separation of arsenic from antimony, tin, copper, lead, mercury,



and iron, and for the estimation of arsenic and iron in arsenide of iron.

The separation of antimony from tin can be effected by taking advantage of the fact that antimony chloride is volatile at  $155-165^{\circ}$  from solutions in which the tin can be rendered non-volatile by the presence of phosphoric acid; the tin can be volatilised subsequently at a somewhat higher temperature by taking advantage of the fact that the addition of hydrobromic acid destroys the restraining action of the phosphoric acid. The authors have attempted to shorten the time required for this separation by utilising the catalysing action of hydrobromic acid from the commencement, but the results are unsatisfactory, since tin distils over with the antimony, the catalysing influence of hydrogen bromide offsetting the restraining effect of phosphoric acid. On the other hand, the use of hydrobromic acid is very advantageous in the separation of antimony or tin alone from other elements, and does not require the absence of nitric acid. Thus, in the separation of antimony and copper, the hydrochloric acid solution of the metals is added to concentrated sulphuric acid (6 c.c.) and phosphoric acid (D 1.78, 7 c.c.) contained in a distillation flask connected with a receiver containing hydrochloric acid. The contents of the flask are heated at  $160^{\circ}$ , and a mixture of concentrated hydrochloric acid (10 volumes) and hydrobromic acid (D 1.78, 1 volume) is added at such a rate that the temperature remains constant. The antimony is completely removed in thirty minutes. The separation of antimony from lead is accomplished similarly.

Tin is quantitatively separated from copper and lead in an analogous manner; the solution of the metals in concentrated hydrochloric acid is treated with sulphuric acid (12 c.c.) and distilled at  $160^{\circ}$  with the regulated addition of the hydrochloric-hydrobromic acid mixture (20 c.c.). The process is complete in half an hour; the tin is precipitated from the distillate as the sulphide and weighed as the oxide. The method can be applied to the estimation of tin in brass.

The separation of antimony and tin from mercury cannot be effected in this manner, since the latter is also partly volatilised.

A novel type of filter tube is described which is constructed by drawing out the end of a piece of wide glass tubing so as to form a stem; a filter disc covered with asbestos rests on the shoulder of the wider tube, which is further provided with a ground-in cap in which a capillary opening is made.

H. W.

#### Early Developments in Organic Macro- and Micro-analysis.

J. V. DUBSKÝ (*Chem. H'ekblad*, 1919, 16, 1482-1493).—The author gives a retrospect of the work of various experimenters in connexion with the analysis of organic substances, and indicates the lines along which research progressed.

W. J. W.

#### Gas Analytical Combustion with Copper Oxide.

E. ORR (*J. Gasbeleucht.*, 1919, 62, 89-90; from *Chem. Zentr.*, 1919, iv, 171-172).—Uncertainties in fractional combustion with copper

oxide arise in consequence of the dissociation,  $\text{CuO} = \text{Cu} + \text{O}$ , which can be eliminated by subsequent, repeated passage of the nitrogen over the material in the quartz tube, which is maintained at a low red heat. Preparation of chemically pure nitrogen by means of phosphorus and heated copper oxide is liable to error, and recourse should be had to the pyrogallol method. Copper oxide does not appear to be suitable for gas analyses in which the carbon dioxide formed by combustion is measured.

H. W.

**Estimation of Carbon Monoxide in Blood.** D. D. VAN SLAKE and H. A. SALVESEN (*Proc. Soc. Exp. Biol. Med.*, 1919, **16**, 140; from *Physiol. Abstr.*, 1919, **4**, 374).—The blood is treated as in the estimation of oxygen by Van Slyke's method. A mixture of carbon monoxide and oxygen with a slight amount of nitrogen is obtained. The oxygen is absorbed by alkaline pyrogallol solution. The residual gas, after a correction has been made for nitrogen, is carbon monoxide.

J. C. D.

**A Micro-method for the Estimation of Calcium in Blood-serum, and other Organic Substances.** D. J. DE WAARD (*Biochem. Zeitsch.*, 1919, **97**, 176—186).—The substances are evaporated and incinerated, and the salts of the ash extracted with dilute hydrochloric acid. The calcium is precipitated from the solution as the oxalate, which is centrifuged, washed, dissolved in dilute acid, and titrated with potassium permanganate. 0.1 Mg. of calcium can be estimated by this method with an error of 4%. S. S. Z.

**A Direct Micro-estimation of Calcium in the Serum.** D. J. DE WAARD (*Biochem. Zeitsch.*, 1919, **97**, 186—189).—All the calcium can be precipitated directly from the serum by means of ammonium oxalate and be estimated by the method described in the preceding abstract. The difference between an estimation carried out on the incinerated serum and on the original serum was only 0.001 mg. of calcium per c.c.

S. S. Z.

**Ferrous Sulphide as an Indicator in Acidimetry and a New Volumetric Method for the Estimation of Zinc.** J. HOUBEN (*Ber.*, 1919, **52**, [B], 1613—1621).—Since the production of ferrous sulphide is prevented by the slightest traces of acids, it is possible to titrate an acid by adding a crystal of pure ferrous ammonium sulphate, passing in well-washed hydrogen sulphide (not enough to saturate the solution), and running in alkali until the black colour of ferrous sulphide is permanent. Experiments with hydrochloric and sulphuric acids on the one hand and alkali hydroxides and carbonates or borax on the other show that the end-point is quite as definite as it is in the case of methyl-orange or phenolphthalein. The only indistinct end-point is found when titrating sulphuric acid with borax, but here the difficulty may be overcome by running in more acid until the black colour just disappears again. The method is obviously useful in the case of coloured liquids, or when working in a bad light.

In the case of zinc salts, hydrogen sulphide completely precipitates zinc as sulphide from the sulphate if the solution is less than 0.2*N*, and from the chloride if the concentration is below 0.067*N*. A titration of the free acid produced would therefore be a means of estimating zinc in its neutral salts, and here the above use of a ferrous salt proves its worth. The solution is saturated with hydrogen sulphide, some ferrous ammonium sulphate is added, and alkali is run in, preferably borax solution, until the white turbidity becomes brown. A "back titration" with an acid is not possible in this case, however, without first filtering the zinc sulphide, as a double zinc-ferrous sulphide is formed which is not quickly broken up. Of course, cobalt and nickel salts must be absent.

Examples of the application of the method to metallic zinc, zinc salts, zinc ash, and blende show that the results approach those obtained by gravimetric analysis very closely, in fact much more so than those given by any other volumetric method. Blende is examined as follows. About 5 grams of the mineral are digested with 40 c.c. of concentrated hydrochloric acid and 40 c.c. of water, the solution filtered and saturated with hydrogen sulphide, filtered again, and diluted to 1000 c.c. with dilute hydrochloric acid. Portions of 50 c.c. are now neutralised with sodium carbonate, using methyl-orange, treated with hydrogen sulphide for half an hour, mixed with ferrous ammonium sulphate, and titrated with borax or sodium carbonate.

The alkalimetric titration of ferric salts may be carried out by employing the same principles.

J. C. W.

#### **Electrometric Analysis with Potassium Ferrocyanide.**

ERICH MÜLLER (*Zeitsch. angew. Chem.*, 1919, **32**, 351—352).—Electrometric titration of lead and zinc salts with potassium ferrocyanide solution is trustworthy, but the method fails in the case of other metals owing to the fact that the precipitates produced do not have definite compositions.

W. P. S.

#### **Colorimetric Estimation of Lead Dioxide in Litharge.**

WALLER V. MORGAN (*J. Ind. Eng. Chem.*, 1919, **11**, 1055). The method depends on the fact that lead dioxide oxidises aniline to aniline-purple, and that the coloration obtained is proportional to the amount of the dioxide present. Five grams of the litharge containing lead dioxide are boiled for one minute with 2 grams of aniline hydrochloride dissolved in 10 c.c. of water and 5 c.c. of concentrated hydrochloric acid; the mixture is then filtered and the coloration exhibited by the filtrate compared with those given under the same conditions by litharge containing known amounts of lead peroxide.

W. P. S.

#### **Complex Internal Salts in Quantitative Analysis. I.**

I. BELLUCCI and A. CHICCIANI (*Gazzetta*, 1919, **49**, ii, 187—216).—The authors summarise and criticise published work on the applications of  $\alpha$ -nitroso- $\beta$ -naphthol and "cupferron" to the separation and estimation of metals.

For the separation of copper, neither of these reagents offers appreciable advantages over ordinary analytical methods, except perhaps for the separation of copper from arsenic and, more particularly, from antimony. For the separation of iron, cupferron is to be preferred to  $\alpha$ -nitroso- $\beta$ -naphthol, chiefly because the ferric precipitate obtained with the former withstands a greater degree of free mineral acidity, and is therefore more easily freed from extraneous metals, and also because the precipitate is less voluminous.  $\alpha$ -Nitroso- $\beta$ -naphthol serves principally as a reagent for cobalt, and also as a reagent for palladium, whilst cupferron acts as a reagent for titanium, zirconium, and vanadium, as well as for iron. The two compounds assume, indeed, the character of general reagents for groups of elements which contain, however, elements quite different from those usually classed together. T. H. P.

**Detection of Cerium.** FR. FEIGL (*Österr. Chem. Zeit.*, [ii, 22, 124—126; from *Chem. Zentr.*, 1919, iv, 592).—Lecoq's reaction is much more distinctly obtained after the addition of a small quantity of an aluminium salt, but is not applicable in the presence of iron. A vivid blue coloration is obtained when cerium dioxide is moistened with a solution of benzidine in acetic acid; other cerous and ceric compounds, with the exception of cerous fluoride, cerous carbonate, and double sulphates of cerium, behave similarly. The reaction is most sensitive when the solution under investigation is made just alkaline with sodium or potassium hydroxide, heated to boiling, filtered, and the filter paper treated with a drop of benzidine solution; 0.02 mg. of cerium per litre can be thus detected. The other metals which belong to the ammonium sulphide group of the rare earths, with the exception of thallium, do not show the reaction. The absence of other oxidising agents and of manganese, cobalt, thallium, and chromate is essential, since the reaction depends on oxidation. Faintly acid solutions of iron also give the reaction; after previous addition of sodium or potassium hydroxide, a coloration is not observed. In the presence of iron, it is advisable to precipitate cerium as the fluoride and to convert the latter by alkali hydroxide into the hydroxide, since precipitated ferric hydroxide carries down notable amounts of cerium, which are thus removed from the sphere of action. H. W.

**Soil Analysis.** F. MÜSTER (*Landw. Versuchs.-stat.*, 1919, 94, 181—189).—For the estimation of iron, aluminium, calcium, magnesium, potassium, and phosphoric acid in a soil, it is recommended that 300 grams of the sample be mixed with 900 c.c. of concentrated hydrochloric acid and shaken occasionally during forty-eight hours; the solution is then decanted, filtered, and 300 c.c. of the filtrate are evaporated with the addition of ammonium chloride. The residue obtained is treated with nitric and hydrochloric acids, again evaporated, this operation is repeated, and the final solution in hydrochloric acid is used, after separation of the silica, for the estimation of the above-mentioned constituents. W. P. S.

**Application of Hæmatoxylin to the Detection of Iron in Tissues.** J. MAWAS (*Compt. rend. Soc. Biol.*, 1919, **82**, 155—158; from *Chem. Zentr.*, 1919, iv, 245).—The author considers that the reaction of hæmatoxylin with ferrous ions is to be ascribed to salt formation, and not, as Macallum assumed, to oxidation. The latter's statement that the reaction only occurs with inorganic iron is incorrect, since iron compounds of the albumins, which are not acted on by hydrogen sulphide or ammonium sulphide, but are affected by potassium ferro- or ferri-cyanide, also show this change. The formation of Prussian-blue is a more delicate test for the presence of iron in tissues; nevertheless, the author has obtained useful results with hæmatoxylin, particularly in certain cases of disease of the eye. The affinity of the hæmatoxylin for the chromatin of the nucleus, whereby a similar coloration is developed, is disadvantageous. H. W.

**Brazilin and its Iron Lakes.** J. MAWAS (*Compt. rend. Soc. Biol.*, 1919, **82**, 158—159; from *Chem. Zentr.*, 1919, iv, 245).—Brazilin is a more sensitive and more rapid reagent than hæmatoxylin (preceding abstract); its aqueous solution, pale red with an orange fluorescence, gives dark brown, insoluble lakes with ferrous salts. In aqueous or alcoholic solution, it colours tissue containing iron dark brown within a few minutes, whilst the nucleus becomes reddish-violet. Differentiation which may be necessary owing to over-colouring is effected with alcohol and chloroform, or, preferably, with alcohol containing 1% of hydrogen chloride. The nucleus becomes practically decolorised, whilst the iron pigment is unaffected; the former again becomes reddish-violet when washed with dilute aqueous alkali. H. W.

**Iodometric Estimation of Iron.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 1565—1568).—The estimation of ferrous iron by means of iodine with addition of a pyrophosphate gives results which are about 3% too low owing to oxidation of the iodine by dissolved oxygen in the solutions. If sulphuric acid and sodium hydrogen carbonate are added to eliminate the oxygen, the error is reduced to 0·8—1%. A more suitable method which gives accurate results is the following: 25 c.c. of 0·1N-potassium bromate and 10 c.c. of 25% phosphoric acid are added to 10 c.c. of 0·1N-ferrous solution to which a few drops of acid have been added. After remaining for five minutes in a stoppered flask, 5 c.c. of potassium iodide and 2 drops of molybdate solution are added, the iodine being titrated after five minutes with thiosulphate.

The purpose of the phosphoric acid is to combine with the ferric ions and prevent them interacting with the potassium iodide, and the molybdate is added to accelerate the reaction of the bromate and iodide. W. J. W.

**Volumetric Estimation of Iron.** J. HOUBEN (*Ber.*, 1919, **52**, [B], 2072—2076. Compare this vol., ii, 53).—The process

permits the estimation of ferrous and ferric iron and free mineral acid in a solution.

A portion of the solution is completely reduced by hydrogen sulphide and titrated with *N*-potassium or sodium hydroxide solution until the dark coloration due to the incipient precipitation of ferrous sulphide is observed, which does not disappear after vigorous shaking; the free acid plus one-third of the acid originally combined with the ferric salt is thereby estimated. A second portion of the solution is reduced with sulphur dioxide (air being completely excluded), most of the excess of the latter is removed by boiling, and the cooled solution is titrated with *N*-alkali as before, after being treated with hydrogen sulphide, which completes the removal of sulphur dioxide. The free acid plus two-thirds of the acid originally united to the ferric iron is thus estimated. The difference between the two titrations multiplied by three gives the number of c.c. of *N*-ferric chloride solution originally present. If this number is subtracted from the smaller of the two burette readings, the difference is the number of c.c. of *N*-acid which were uncombined in the solution. The ferrous salt is estimated in the usual manner. Test analyses show the method to have a high degree of accuracy.

H. W.

#### Separation of Iron, Aluminium, Chromium, Glucinum, Titanium, and Zirconium by the Sodium Carbonate Method.

P. WENGER and J. WURMANN (*Ann. Chim. anal.*, 1919, [ii], 1, 337—339).—A method described previously by Wenger and Wunder (*A.*, 1912, ii, 687) may be applied when the mixture contains titanium or zirconium, but not both. After fusion with sodium carbonate, the insoluble iron and zirconium oxides may be treated with hydrochloric acid (1:1), in which the zirconium oxide is insoluble. In the absence of zirconium, iron and titanium may be separated by one of the known methods, even in the presence of glucinum. [See, further, *J. Soc. Chem. Ind.*, 1920, 46A.]

W. P. S.

#### A New Method for the Volumetric Estimation of Nickel.

JOSEF HOLLUTA (*Monatsh.*, 1919, 40, 281—291).—The process depends on the fact that, when a nickel salt reacts with dimethylglyoxime, acid is liberated, which is estimated by titration with alkali in the presence of phenolphthalein or methyl-red.

The standard *N*/50-solution is prepared by dissolving 4.6400 grams of pure dimethylglyoxime in the requisite quantity of 97% alcohol (300—400 c.c.); 20 c.c. of *N*-potassium hydroxide solution are added with constant shaking, and the solution is diluted to 1000 c.c. with distilled water free from carbon dioxide and filtered after twenty-four hours from any slight precipitate of potassium carbonate. (The alcohol used must be free from aldehyde and neutral in reaction.) The alkali content of the solution is checked by titration with standard acid, using phenolphthalein or methyl-red as indicator. The nickel solution under examination is diluted

to the required extent, and exactly neutralised with  $N/10$ - or  $N/50$ -potassium hydroxide solution. 2–5 C.c. of the standard solution are added, and, after vigorous agitation, the solution is gently warmed, whereby the precipitate is caused to collect, leaving a clear liquor; the standard solution is then gradually added with frequent agitation until the solution acquires a permanent, pale pink coloration. In consequence of the bulky nature of the nickel precipitate, the amount of the metal in the solution should not exceed 0.03 gram.

The method is particularly advantageous in dealing with very small quantities of nickel, and titration can readily be effected with  $N/100$ -solutions if methyl-red is substituted for phenolphthalein as indicator. The results are not affected by the presence of the alkali salts of strong acids. Further details are promised in a subsequent communication.

H. W.

**Iodometric Estimation of the Chromic Acid in Lead Chromate.** MAN GRÖGER (*Zeitsch. anorg. Chem.*, 1919, 108, 267–272).—The iodometric method of estimating chromic acid has not hitherto been used for lead chromate on account of the impossibility of completely decomposing the chromate by means of dilute sulphuric acid. Dilute hydrochloric acid dissolves lead chromate completely, but hydrochloric acid has a reducing action on chromic acid, with liberation of free chlorine, and has therefore not been used to dissolve lead chromate. It is now found, however, that if the hydrochloric acid is sufficiently dilute, its reducing action is negligible. Experiments showed that when acid of 1.25*N* strength or less was used, in the proportion of 25HCl to 1 mol. of chromate, no reduction took place after boiling the solution for three hours. With stronger hydrochloric acid, the rate of reduction increased rapidly with the concentration of the acid. For carrying out an analysis, about 0.3 gram of lead chromate is dissolved in 50 c.c. of 1.25*N*-hydrochloric acid by gently heating. The solution is cooled, 1 gram of potassium iodide added, allowed to remain for ten minutes, diluted with 100 c.c. of water, and the free iodine titrated with sodium thiosulphate. There is no need to filter off the precipitated lead iodide, as the colour of this does not interfere with the end-point. After the end of the titration, free iodine again appears after a short time. This is due to atmospheric oxidation of hydriodic acid, a reaction which appears to be catalysed by the lead iodide present. The results obtained by this method are generally about 0.5% too high.

E. H. R.

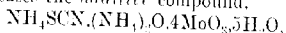
**Detection of Molybdenum by means of Xanthic Acid.** J. KOPPEL (*Chem. Zeit.*, 1919, 43, 777–778).—Molybdenum compounds give a characteristic red to plum-coloured reaction with xanthic acid, which was first described by Siewert (*Zeitsch. ges. Naturw.*, 1864, 23, 5). The test is preferably applied by acidifying the solution with a mineral acid, after the addition of a trace of solid potassium xanthate, and is capable of detecting molybdenum in a solution containing 0.0000064 gram per c.c. The reaction is

weaker when phosphoric, formic, or acetic acid is used for the acidification, and much weaker with salicylic acid, whilst when oxalic, citric, or tartaric acid is used, there is little, if any, coloration. Analogous xanthic compounds are formed by copper, iron, cobalt, nickel, etc., but the colorations do not interfere with the molybdenum test. Vanadic acid forms a yellow compound and uranic acid a brown compound, which, like the molybdenum compound, are soluble in ether and other organic solvents. Tungstic acid, if present in very large preponderance, may interfere with the test. The molybdenum compound may be obtained as a black oil by mixing a solution of 2 grams of ammonium paramolybdate with 1 gram of potassium xanthate. When vigorously stirred, this oil solidifies, forming black crystals with green surface reflections. The mean analyses of Siewert's solid preparation agree with the formula  $\text{MoO}_3(\text{OEt}(\text{C} \cdot \text{S} \cdot \text{S} \cdot \text{H}))_2$ . [See also *J. Soc. Chem. Ind.*, 1920, January.]

C. A. M.

### Colour Reactions of Molybdenum and Tungsten. II.

G. A. BARBIERI (*Atti R. Accad. Lincei*, 1919, [v], 28, i, 390-392. Compare A., 1919, i, 549).—According to Péchard (A., 1894, ii, 319), replacement of the hydrochloric or sulphuric acid used in Braun's reaction by acetic acid results in the formation of a yellow coloration, and, with concentrated solutions, of a yellow, crystalline precipitate, due to conversion of the molybdate into trimolybdate, and union of this with the thiocyanate present to form an additive compound, for instance,  $\text{KCNS} \cdot \text{K}_2\text{O} \cdot 3\text{MoO}_3 \cdot 4\text{H}_2\text{O}$ . On repetition of Péchard's reaction with ammonium thiocyanate and ammonium permolybdate or tri- or tetra- or normal molybdate, the author finds that in all cases the *additive* compound,



is formed, and in no case an additive compound of the trimolybdate. From potassium trimolybdate and thiocyanate in presence of acetic acid, the corresponding *compound*,  $\text{KSCN} \cdot \text{K}_2\text{O} \cdot 4\text{MoO}_3 \cdot 5\text{H}_2\text{O}$ , is formed; both potassium and ammonium compounds form yellow, acicular crystals.

Ammonium tetramolybdate,  $(\text{NH}_4)_2\text{O} \cdot 4\text{MoO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , may be obtained by the action of acetic acid on ammonium permolybdate in aqueous solution (compare Junius, A., 1905, ii, 825).

T. H. P.

### Qualitative and Quantitative Test for Molybdenum in Steel and Iron.

SIEGFRIED LAURENS MALOWAN (*Zeitsch. anorg. Chem.*, 1919, 108, 73-80).—A specific and very sensitive test for molybdenum is given by xanthic acid. The test is best carried out with freshly prepared xanthate solution in the following manner. Absolute alcoholic potash is shaken with excess of carbon disulphide until no more of the latter is dissolved. To the solution so obtained, 30% acetic acid is added until it shows a slight yellow turbidity, and the reagent is added drop by drop to the solution to be tested. If molybdenum is present, an intense red colour



develops, which is quite stable in water, and the intensity of which is proportional to the quantity of molybdenum present. The sensitiveness of the reaction is such that 0.000005 gram of molybdenum in 0.0007% solution can be detected with certainty in presence of other elements. The coloured product is readily soluble in ethyl or amyl alcohol, ether, or chloroform, less easily in petroleum and benzene. It is readily extracted from its reddish-violet ethereal solution by alkalis, from which acids precipitate it. The ethereal solution decomposes on keeping, with formation of molybdenum sulphide. The reaction is not given by vanadium, tungsten, titanium, or uranium; chromates give a dark coloration with xanthic acid, and should be reduced, if present, before the test is made. The reaction can be used for the colorimetric estimation of molybdenum, the coloured product being extracted with a mixture of 65% ether and 35% light petroleum, and a mixture of 30% ether and 70% light petroleum used for dilution for comparison with the standard solution. If pure ether is used, decomposition takes place too rapidly for accurate determinations to be made. E. H. R.

**Colorimetric Method for the Estimation of Small Quantities of Uranium.** MÜLLER (*Chem. Zeit.*, 1919, 43, 739—740).—The method depends on the red coloration obtained when a uranyl salt is treated with sodium salicylate; the coloration yielded by any uranyl salt solution is compared with that produced by a known amount of uranium under the same conditions. Free mineral acid, acetic acid, iron, alcohol, or acetone must not be present, but neutral alkali salts do not interfere. The method is suitable for the estimation of uranium in solutions containing as little as 0.02% of the metal. W. P. S.

**Estimation of Zirconium by the Phosphate Method.** G. E. F. LUNDELL and H. B. KNOWLES (*J. Amer. Chem. Soc.*, 1919, 41, 1801—1808).—Zirconium can be quantitatively precipitated as secondary zirconium phosphate in cold or tepid solutions containing from 2% to 20% by weight of sulphuric acid, provided that a ten- to one hundred-fold excess of the precipitant, diammonium hydrogen phosphate, is used. Hydrolysis, which occurs when the phosphate precipitate is washed with water, can be almost entirely avoided by the use of a cold 5% ammonium nitrate solution for washing. Zirconium pyrophosphate, for which the  $ZrO_2$  factor is 0.4632, is obtained on ignition of a secondary zirconium phosphate which has been washed with ammonium nitrate solution. No definite composition can be ascribed to the compound resulting when secondary zirconium phosphate which has been washed with water is ignited. Zirconium can be quantitatively separated as phosphate in a 20% sulphuric acid solution from iron, aluminium, chromium, cerium, and thorium. The separation from titanium can also be effected provided hydrogen peroxide is present. J. F. S.

**Gas-analytical Separation of Acetylene, Ethylene, and Benzene.**

W. D. TREADWELL and F. A. TAUBER (*Helv. Chim. Acta*, 1919, 2, 601—607).—The quantitative absorption of acetylene from mixtures containing it, together with ethylene and benzene vapour, is conveniently effected with a solution of mercuric cyanide (20 grams) in 2*N*-sodium hydroxide solution (100 c.c.); the gas is shaken with the mixture (5 c.c.) for one to two minutes, at the end of which the acetylene is completely absorbed, whilst ethylene and benzene vapour are unaffected.

A solution of mercuric nitrate (20 grams) in 2*N*-nitric acid (100 c.c.) which has been saturated with sodium nitrate is recommended for the absorption of ethylene in the presence of benzene vapour; the gas is shaken with 5—10 c.c. of the solution for two to three minutes. Propylene appears to behave similarly to ethylene, since it is indifferent to alkaline mercuric cyanide solution, whilst readily absorbed by mercuric nitrate solution.

H. W.

**Dehydrogenation of Hydrocarbons by means of Palladium-black.**

JENŐ TAUSZ and NIKOLAUS VON PUTNOKY (*Ber.*, 1919, 52, [B], 1573—1583). Zelinski has shown that *cyclohexanes* are converted into benzene hydrocarbons by exposing them to the action of palladium-black at 300°, whereas hexane and *cyclopentanes* are unchanged (*A.*, 1913, i, 167). This seemed to offer a process whereby *cyclohexanes* could be estimated in the presence of paraffins, and a method has now been developed which gives satisfactory results within certain limits.

The first difficulty to be overcome was the preparation of a sufficiently active catalyst, for Zelinski's agent is spoilt by mixtures of paraffins and *cyclohexane* long before the latter is completely dehydrogenated. In the reduction of palladium solutions, it is usual to employ formic acid, any excess being destroyed by the palladium-black itself. It seemed possible, therefore, that the activity of the catalyst would suffer in such a treatment, and as it was found that the activity towards formic acid is parallel to the activity towards *cyclohexane*, it was decided to use no more than the theoretical quantity of the reducing agent. This has the desired effect, the catalyst being much more active. For example, two specimens of 1 gram each, prepared by Zelinski's method, produced 1.8 and 11.2 c.c. of gas from formic acid, but ten samples made by the new process, which is described in detail, gave on an average 458 c.c., one portion developing as much as 840 c.c.

With such an active catalyst, the quantitative dehydrogenation of *cyclohexane* in various mixtures with hexane may be easily realised; but then another disturbing factor appears, namely, that at 300° the saturated paraffins themselves are to a certain extent converted into unsaturated hydrocarbons by palladium black. The small amount of hydrogen set free by the paraffins, however, reaches a constant volume after an hour or two, and although a little more gas is liberated when the catalyst is renewed, an equilibrium

is soon established. A similar equilibrium is reached when the olefines are heated with an excess of hydrogen, that is, the hydrogenation is never quite complete. The volume of hydrogen produced by the paraffins is relatively small compared with the yield from the *cyclohexanes*, so, within certain limits, the proportion of the latter hydrocarbons in a mixture can be gauged from the amount of hydrogen liberated. The limit is generally about 1% of cyclic hydrocarbon, but in some experiments it was as low as 0.5%. For mixtures containing less than this, only the chemical proof of the presence of benzene will suffice. The reaction with trioxymethylene and sulphuric acid is recommended.

For quantitative purposes, a special apparatus is described. The catalyst (12 grams) is contained in a tube heated in a simple electric furnace, and the vapour is continually circulated. The volume of oil employed varies from 10 c.c. for rich mixtures to 100 c.c. In the experiments described, the following volumes of hydrogen were produced by 1 c.c. of hydrocarbon at 300° (or 270° in the case of the methyl derivatives): *cyclohexane*, 614 c.c.; *methylcyclohexane*, 618 c.c.; 1:3-dimethyl*cyclohexane*, 504 c.c.; *isopentane*, 38 c.c.; *n*-hexane, 40.8 c.c. (after renewing the catalyst five times); *n*-heptane, 32.5 c.c.; *n*-octane, 36 c.c.

As an important application of the method, the analysis of a sample of hexane, b. p. 69–71°, from American petroleum is recorded. Whereas 30 c.c. of synthetic *n*-hexane gave only 338 c.c. of hydrogen, 30 c.c. of the natural oil yielded 446 c.c. under exactly the same conditions. This corresponds with 2.4% of *cyclohexane* in the sample, and actually 0.5592 gram of pure dinitrobenzene was obtained from the dehydrogenated 30 c.c. of oil.

J. C. W.

### Criteria of the Degree of Purity of Commercial Toluene.

JOHN SCOTT LUMSDEN (T., 1919, 115, 1366–1372).

**Differentiation of Methyl and Ethyl Alcohols.** PANNWITZ (*Pharm. Zentr.-b.*, 1919, 60, 441–442). Although crystallised copper sulphate is insoluble in ethyl alcohol and dissolves in methyl alcohol to give a blue solution, this test is useless for distinguishing methyl alcohol from ethyl alcohol, owing to the fact that a small quantity of water destroys the blue colour of the methyl alcohol solution. The quantity of added water must be increased to 35% by vol. before the blue colour reappears, and at this dilution ethyl alcohol also begins to dissolve copper sulphate. The same effects are noticed when ferrous sulphate is used in place of copper sulphate. The borax flame test for methyl alcohol also fails when water is present.

W. P. S.

**Influence of the Presence of Trimethylene Glycol on the Estimation of Glycerol by the Zeisel *iso*Propyl Iodide Method.** C. A. KOJAHN (*Ber.*, 1919, 52, [B], 1454–1460).—Although trimethylene glycol produces no silver iodide precipitate when

digested by itself in the Zeisel apparatus at 120–125°, it does so behave when added to glycerol. In fact, the excess of silver iodide corresponds with the amount of *s*-di-iodopropane produced if the quantity of trimethylene glycol is small. As a consequence, Zeisel's method is not applicable to the estimation of fermentation glycerol (the German "protol"-glycerol), for this contains trimethylene glycol.

J. C. W.

**Chromatic Reactions of Formaldehyde with certain Aromatic Compounds.** ARTURO ROSSI (*Boll. Chim. Farm.*, 1919, 58, 265–270).—Colorations, which are not necessarily distinctive of the aldehyde, are given by formaldehyde in 0.1 or 0.001% aqueous solution, when added to sulphuric acid containing a trace of certain aromatic compounds in solution. Applied as a zone reaction, the following colorations are obtained: *Gallic acid*, a reddish-brown ring, and, on shaking the tube, a green liquid changing to greyish-green. *Tannic acid*, a reddish-brown ring, and a liquid bluish-green at the bottom, but subsequently brownish-red throughout. *Pyrogallol*, a light rose-coloured ring, and liquid. The test is capable of detecting 0.00001% of formaldehyde. *Salicylic acid*, a light rose-coloured ring and solution. *Catechol* and *resorcinol*, various red rings and liquids.  $\beta$ -*Naphthol*, a violet-red ring, and brownish-black liquid with green fluorescence. *Benzonaphthol*, similar colour reactions. *Phenyl salicylate*, carmine-red ring and reddish-yellow liquid, becoming pink on dilution. *Phenolphthalein*, no ring, but an orange liquid changing to carmine-red on shaking. Dilution with water causes a carmine-red precipitate to separate.

C. A. M.

**Estimation of Formaldehyde in Blood.** E. SALKOWSKI (*Biochem. Zeitsch.*, 1919, 97, 129–135).—The protein of the blood is hydrolysed with gastric juice. The hydrolysed mixture is distilled and *N*/10-iodine added to the distillate. The residual iodine is then titrated with thiosulphate. The formaldehyde found amounted to only 85.73% of the quantity added to the blood.

S. S. Z.

**Estimation of Acetone and Acetoacetic Acid with Autenrieth's Colorimeter.** H. SCHALL (*Münch. med. Woch.*, 1919, 66, 812–814; from *Chem. Zentr.*, 1919, iv, 562).—Description of the application of Autenrieth's colorimeter to the colorimetric estimation of acetone according to Legal and to the estimation of acetoacetic acid. Gerhard's iron chloride reaction is suitable for the estimation of considerable concentrations of the latter (above 0.5%), whilst, at greater dilutions, Rimini's ethylenediamine test is used. The former has the advantage of easy manipulation and constancy of colour, whilst the latter is more sensitive and gives a pure tint which, however, rapidly loses in intensity. Empirical solutions of dyes are used as standards. When acetone and acetoacetic acid are present simultaneously, the estimation of acetone requires

the correction of a factor, since acetoacetic acid gives a positive Legal's reaction which is 5.55 as intense as that of acetone.

H. W.

**An Acetoneurometer.** A. ADLER (*Münch. med. Woch.*, 1919, 66, 722—723; from *Chem. Zentr.*, 1919, iv, 398).—A colorimetric method of estimating acetone is described which is based on Legal's test. A mixture of urine (10 c.c.), sodium hydroxide solution (20%, 1 c.c.), and sodium nitroprusside solution (33%, 0.5 c.c.) is well shaken, and acetic acid (20 drops) is added. The colour is compared with that given by mixing Neutral-red, New-blue, and Diamond-phosphine. Solutions of the dyes of the following concentrations are prepared: Neutral-red, 1:1000; New-blue, 1:1000; Diamond-phosphine D, 1:100. Ten c.c. of the first, 3 c.c. of the second, and 0.6 c.c. of the third solution are mixed with water, 5 c.c. (solution I), and correspond with 0.1% of acetone. Ten c.c. of solution I diluted with an equal volume of water correspond with 0.08% of acetone; 5 c.c. of solution I with 10 c.c. of water are equivalent in colour to 0.05% of acetone; 5 c.c. of solution I with 15 c.c. of water correspond with 0.01% of acetone. Five c.c. of a solution of neutral-red (10 c.c.), new-blue (1 c.c.), and diamond-phosphine (0.1 c.c.) with water (50 c.c.) correspond with 0.005% of acetone. The solutions are placed in tubes similar to those used in the experiment, which are subsequently sealed. The five standards are in practice sufficient for ascertaining the acetone content of a urine. H. W.

**Methylene-blue as a Reagent for the Detection of Sugar in Urine.** F. URZ (*Süddeut. Apoth. Zeit.*, 1919, 59, 280—281; from *Chem. Zentr.*, 1919, iv, 212—213).—According to the author's observations, urines which contain sugar always give a positive reaction with solutions of methylene-blue, even when Lieber's modification of the test is used. Aqueous solutions of dextrose behave similarly, but sucrose, carbamide, uric acid, and saliva do not give the reaction. Milk behaves similarly to urine containing sugar. Whilst aqueous solutions of hexamethylenetetramine do not react with methylene-blue, the urines of patients to whom the drug has been administered behave similarly to saccharine urines, but do not give a positive result with Fehling's solution or Nylander's reagent. Normal urines, free from sugar, also give a positive reaction with methylene-blue when they have been preserved for some days and are partly decomposed, and this is particularly noticeable if they have been rendered alkaline with potassium hydroxide. Artificial gastric juice and glycuronic acid are also able to decolorise methylene-blue. The substance, therefore, is not a suitable reagent for the detection of sugar in urine.

H. W.

**Rapid Method for the Estimation of Sugar in Urine.** OTTO MAYER (*Arch. Hyg.*, 1919, 88, 184—197; from *Chem. Zentr.*, 1919, iv, 211—212).—The detection of sugar in urine is best carried out by Trommer's test, for the performance of which, as also for Fehling's and Nylander's reactions, practical directions are given.

The estimation of sugar is effected in the following manner: urine (10 c.c.) is placed in a 100 c.c. stoppered measuring cylinder, sodium hydroxide (15%, 10 c.c.) is added, and the solution is diluted to 50 c.c. with water; copper sulphate solution (25 grams per litre) is gradually added with gentle shaking until the precipitate, which denotes the end of the reaction, practically completely redissolves on vigorous agitation, leaving only a just perceptible but permanent turbidity, which slightly increases in course of time. Under these conditions each c.c. of copper sulphate solution corresponds with 0.1% of dextrose. If the urine contains more than 4% of sugar it is preferable to take only 5 c.c., whilst if the content is 0.5–1% 20 c.c. may be measured out. Separation of alkaline earth phosphates from urines which have been treated with alkali and diluted from 2.5 to 10 times occurs only when these are present in exceptional quantity. In this case, since the sensitiveness of the end-point may be greatly reduced, it is advisable to treat 20 c.c. of the urine with 20 c.c. of sodium hydroxide solution, to filter the solution after dilution to 100 c.c., and to perform the titration with 50 c.c. of the clear filtrate.

For the detection of acetone, powdered sodium nitroprusside (0.05–0.1 gram) is shaken with about 10 c.c. of urine, about 1 c.c. of sodium hydroxide (15%) is added to the solution, which is then acidified with acetic acid (30%, 2 c.c.). In this form the test is so sensitive that distillation is only necessary with such urines as are deeply coloured or contain only small amounts of acetone. The most suitable reagent for the detection of acetoacetic acid is a mixture of liquor ferri sesquichl. (5 c.c.) and sodium chloride solution (1:3, 95 c.c.), the reaction being performed as a ring test. H. W.

**Volumetric Estimation of Sugar in Milk.** J. L. MAYER (*J. Amer. Pharm. Assoc.*, 1919, 8, 551–553).—Benedict's method for the estimation of dextrose in urine as modified by the author was applied to the estimation of lactose in milk. The results were trustworthy.

CHEMICAL ABSTRACTS.

**[Estimation of Invert-sugar by Fehling's Solution.]** J. D. VAN LEEUWEN (*Chem. Weekblad*, 1919, 16, 1425–1426).—In the titration of invert sugar solution with Fehling's solution, dilution of the latter with four times its volume of magnesium sulphate solution (0.5 gram per litre) causes the precipitated cuprous oxide to settle rapidly, and thus gives a clear solution for testing with potassium ferrocyanide and acetic acid; the solution must be cooled for this test. W. J. W.

**Estimation of Carbamide by means of Sodium Hypobromite.** E. DEKEUWER and L. LESCOEUR (*Compt. rend. Soc. Biol.*, 1919, 82, 445–447; from *Chem. Zentr.*, 1919, iv, 350).—In the estimation of pure carbamide by bromine and alkali hydroxide, a slight deficit is always observed which has about the same magnitude when calculated from the nitrogen evolved or from the bromine used; the error is doubled when the calculation is based on the

amount of carbon dioxide formed. The course of the reaction appears to depend on the relative quantities of alkali and carbamide. A factor can be applied based on the results obtained. In the estimation of carbamide in urine, high results are obtained when the calculation is based on the bromine which is utilised (particularly in the case of urines containing sugar), since bromine is also used in the oxidation of substances other than carbamide. The results deduced from the amounts of nitrogen and carbon dioxide formed respectively generally agree well among themselves; in the case of urines containing sugar, the values calculated from carbon dioxide are lower than those reckoned from nitrogen.

H. W.

**Estimation of Carbamide in Blood and Urine.** C. BRAHM (*Deut. med. Woch.*, 1919, **45**, 803; from *Chem. Zentr.*, 1919, iv, 442).—A criticism of Citron's method of estimating carbamide. The latter is not quantitatively decomposed by sodium hypobromite according to the scheme:  $\text{CO}(\text{NH}_2)_2 + 3\text{NaBrO} = 13\text{NaBr} + \text{CO}_2 + 2\text{H}_2\text{O} + \text{N}_2$ , since a proportion of the nitrogen is retained as nitric acid or cyanuric acid. In the author's opinion all methods which are based on the reaction between carbamide and sodium hypobromite are to be rejected. The form of apparatus proposed is also open to many objections.

H. W.

**Estimation of Carbamide in Urine by means of Urease.** ARNOLD HAHN (*Deut. med. Woch.*, 1919, **45**, 911—912); from *Chem. Zentr.*, 1919, iv, 562—563).—The author's method has been modified by Horváth and Kadletz by the introduction of a receiver containing acid; the alteration is regarded as adding an unnecessary complication to the process.

H. W.

**Detection of Hydrocyanic Acid in a Case of Poisoning. Its Post-mortem Transformation into Sulphocyanic Acid.**

L. CHELLE (*Compt. rend.*, 1919, **169**, 852—854. Compare A., 1919, ii, 529, 530). A dog was poisoned by administering potassium cyanide and an autopsy immediately performed, the various organs being divided up and kept in stoppered sterile flasks for various lengths of time. Using the methods previously described (*loc. cit.*), hydrocyanic acid as such, but no thiocyanic acid, was detected after two hours in the brain, lungs, and blood, but not in the liver. After eight days no hydrocyanic acid as such could be detected in any of the organs or the blood, but thiocyanic acid was found in the blood, lungs, and brain, but not in the liver. Further, the amount of thiocyanic acid found in the lungs and brain, but not in the blood, corresponded with far more than the amount of hydrocyanic acid found at the end of two hours. This is explained on the grounds that a certain amount of hydrocyanic acid becomes enclosed in the cells in the first few hours after death and is not set free by the methods of estimation used, but after eight days, as a result of

putrefaction and consequent cytolysis, it is all liberated by the reagents and thus estimated. W. G.

**Estimation of Ferricyanide and Ferrocyanide.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 1618—1626).—The author has investigated the iodometric estimation of potassium ferricyanide. The acidity of the solution has an appreciable influence on the reaction; if the concentration is sufficiently high, accurate results are obtained after allowing the solutions to remain for only half a minute. Rupp's method for the estimation of ferrocyanide is inaccurate. An outline is given of the theoretical interpretation of the iodometric estimation of ferri- and ferro-cyanide. The reducing action of ferrocyanide is increased by rise of temperature.

W. J. W.

**Proteinogenous Amines. II. A Micro-chemical Colorimetric Method for Estimating Iminazole Derivatives.** KARL K. KOESSLER and MILTON T. HANKE (*J. Biol. Chem.*, 1919, **39**, 497—519).—The method depends on the colour reaction between compounds containing the iminazole ring and sodium *p*-diazobenzenesulphonate. It can be applied directly to practically any iminazole derivative, gives equally good results whether applied to pure solutions or mixtures, and is capable of estimating with a fair degree of accuracy as little as 0.00001 gram of any of the iminazoles. The iminazole derivative is added under certain conditions to a mixture of sodium carbonate and the *p*-diazobenzenesulphonic acid in one cup of a Duboscq colorimeter, and the height of liquid in this cup is set at 20 mm. The other cup is filled with an appropriate indicator solution, and the height varied until the colours match. From tables which have been prepared, the amount of the iminazole derivative can be read off. Certain substances interfere with the method, notably ketones, alcohols, ammonium salts, and proteins. Animal charcoal must not be used to decolorise solutions which it is desired to test for iminazole derivatives, as loss by adsorption occurs. J. C. D.

**Proteinogenous Amines. III. A Quantitative Method for Separating Histamine from Histidine.** KARL K. KOESSLER and MILTON T. HANKE (*J. Biol. Chem.*, 1919, **39**, 521—538).—The colorimetric process described in the preceding abstract may be utilised for estimating certain components of mixtures of iminazole derivatives. A mixture of these derivatives, such, for example, as that which is formed by the action of bacteria on histidine in the presence of salts and dextrose, is treated with sufficient sodium hydroxide to make the whole a 20% solution of alkali. This solution is extracted repeatedly with amyl alcohol, whereby the histamine, ammonia, methyliminazole, and other amines are removed. This extract is termed the histamine fraction, whilst the residual liquid containing histidine, iminazole, propionic, acetic and lactic acids is called the histidine fraction. The amount of histidine can be determined by an estimation of the



amino-nitrogen in the second fraction. A colorimetric estimation on the same fraction will indicate whether there are other iminazole derivatives present other than histidine.

The histamine and methyliminazole are extracted from the amyl alcohol by 1.0*N*-sulphuric acid, and a colorimetric estimation will give on this extract an indication of the total iminazole substances present. The methyliminazole may be estimated directly by the fact that it is volatile in steam. The colorimetric estimations on these two fractions will give by difference the amount of histamine present.

J. C. D.

**Direct Estimation of Non-amino-nitrogen in the Products of Protein Hydrolysis.** ALMA HILLER and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1919, **39**, 479—488).—An extension of the method of protein analysis introduced by Van Slyke (A., 1915, ii, 851). The filtrate from the phosphotungstates of the diamino-acids, representing 2 or 3 grams of protein, is concentrated to 150 c.c. Portions of this solution are used for estimations of the total nitrogen and amino-nitrogen, as described in the original paper. Of the residue, 100 c.c. are measured into a separating funnel of 500 c.c. capacity, and are rendered free from phosphotungstic acid by extraction with amyl alcohol-ether mixture in the presence of hydrochloric acid. The solution is concentrated in a vacuum to about 50 c.c., and washed into a 100 c.c. volumetric flask. Of this solution, 20 c.c. portions are used for the non-amino-nitrogen estimation. Each portion is placed in a small Kjeldahl flask with 1.2 c.c. of 30% sodium nitrite and 5 c.c. of concentrated hydrochloric acid. When deamination is completed, the solution is neutralised to alizarin with 10% sodium hydroxide and reduced with zinc-copper couple. After making alkaline with magnesium oxide, the ammonia formed by the reduction is removed by boiling, and residual nitrogen is estimated by the Kjeldahl process. The results by this direct method agreed closely, in analyses of caseinogen and gelatin, with the results obtained indirectly by the original procedure.

J. C. D.

**Apparatus for Rapid Gastric Analysis, together with a Method for the Preservation of Starch Solution.** RAYMOND J. MILLER (*J. Ind. Eng. Chem.*, 1919, **11**, 963—964).—A convenient arrangement of burettes, indicator reservoirs and delivery tubes, an automatic pipette, etc., attached to one stand, and intended for the estimation of total acidity, free acidity, and amino-acid nitrogen (formaldehyde method) in gastric fluids. The starch solution is preserved under a layer of liquid "petrolatum," with or without the addition of a small quantity of toluene.

W. P. S.

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- I. 0.4973 gave 0.0877 HgS and 0.0804  $\text{Al}_2\text{O}_3$ . Hg=15.19;  
Al=9.51.  
0.4348 gave 0.6548 AgCl. Cl=36.43.  
II. 0.4407 gave 0.0777 HgS and 0.0790  $\text{Al}_2\text{O}_3$ . Hg=15.20;  
Al=8.57.  
0.5995 gave 0.8831 AgCl. Cl=37.25.  
 $4\text{AlCl}_3, \text{HgCl}_2, 28\text{H}_2\text{O}$  requires Hg=15.27; Al=8.25; Cl=37.96;  
 $\text{H}_2\text{O}$ =38.52 per cent.

*Cryoscopic Determination of the Molecular Weight.*

Solvent, 15.7251 grams of water.

	Solute.	$\Delta t$ .	M.W.
1 .....	0.0963	-0.087°	130.84
2 .....	0.3077	-0.277	130.94
3 .....	0.6055	-0.515	137.10

The value found in this way approximates to one-tenth of the molecular weight, namely, 1309. In aqueous solution, the double salt is decomposed, as the solution is found to be distinctly acid. Since the compound  $4\text{AlCl}_3, \text{HgCl}_2, 28\text{H}_2\text{O}$  is completely hydrolysed to hydrochloric acid, aluminium hydroxide, and mercuric chloride, the observed molecular weight ought to be one-twelfth of 1309, as the lowering of the freezing point, due to the aluminium hydroxide and mercuric chloride, is quite negligible. This anomaly is difficult to explain, and the molecular weight determination does not, therefore, furnish much evidence as to the true molecular weight of the double salt in solution.

I avail myself of this opportunity to express my sincere thanks to Sir Prafulla Chandra Rây for his helpful interest and encouragement in this work.

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CALCUTTA.

[Received, June 6th, 1919.]

# XI.—Acyl Substituted isoThiohydantoins.

By AUGUSTUS EDWARD DIXON and RAYMOND THOMAS JOACHIM  
KENNEDY.

CONCERNING the acyl substituted isothiohydantoins, practically the whole of our knowledge, embodied in two papers, one by Wheeler and Johnson (*Amer. Chem. J.*, 1902, **28**, 121) and the other by Johnson, Wallbridge, McFarland, and Cramer (*J. Amer. Chem. Soc.*, 1903, **25**, 483), may be summarised as follows. isoThiohydantoins containing an aryl group, R, in the ring, by treatment with thiolacetic acid or with acetic anhydride, yield acetyl derivatives of the form  $\text{MeCO}\cdot\text{N}:\text{C} \begin{smallmatrix} \text{NR}\cdot\text{CO} \\ \text{S} \text{---} \text{CH}_2 \end{smallmatrix}$ , the phenylic member of this class being producible also from either phenylisothiohydantoic acid or thiocyanacetanilide by means of acetic anhydride. Further, ordinary  $\beta$ -naphthylisothiohydantoin gives with acetic anhydride a derivative,  $\text{C}_{10}\text{H}_7\cdot\text{N}:\text{C} \begin{smallmatrix} \text{N}(\text{COMe})\cdot\text{CO} \\ \text{S} \text{---} \text{CH}_2 \end{smallmatrix}$ , the corresponding *o*- or *p*-tolylisothiohydantoin, under like treatment, affording a diacetyl derivative.

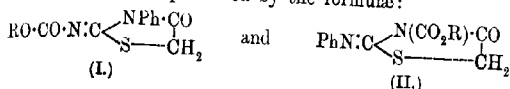
No purely acidic substitution derivative of isothiohydantoin seems yet to have been described. It was found, too, by Dixon and Taylor (*T.*, 1912, **101**, 558) that *ab*-acetylphenylthiocarbamide, when heated with chloroacetyl chloride, yields ordinary phenylisothiohydantoin, the acyl substituent of the thiocarbamide being expelled in the form of acetyl chloride. Similar results were observed with tri-substituted thiocarbamides containing the acetyl, the benzoyl, or the carbethoxy-radicle, together in each case with two hydrocarbon residues.

Such tri-substitution derivatives are not particularly stable. More recent investigation has shown that less highly substituted thiocarbamides containing the group  $\cdot\text{CO}\cdot\text{OR}$  (where R = alkyl or aryl), by means of chloroacetyl chloride are transformable into isothiohydantoins without the loss of that group. Thus, for example, carbethoxyisothiohydantoin may be obtained from carbethoxythiocarbamide, or a phenylcarbethoxy-analogue from *ab*-phenylcarbethoxythiocarbamide.

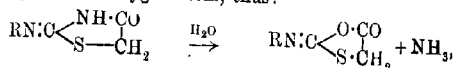
Consistently with the observations of Dixon and Taylor (*loc. cit.*) it has been found that ethyl chloroacetate, in alcoholic solution, fails to attack the mono-substituted carboalkyloxythiocarbamides; if, however, calcium carbonate is added to the mixture, interaction takes place, with the formation of the corresponding mono-substi-

tuted isothiohydantoin. With di-substituted thiocarbamides,  $\text{RO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$ , or with mono-substituted carboaryloxythiocarbamides, however, ethyl chloroacetate does not react, either directly or in the presence of calcium carbonate.

So far as their method of production is concerned, the carboalkyloxyisothiohydantoin referred to above might have either (or both) of the configurations represented by the formulae:

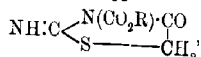


When hydrolysed by means of hot dilute hydrochloric acid, they yield carbon dioxide, ammonium chloride, and 'phenyldioxythiazole.' Now, Dixon has shown (T., 1897, 71, 623) that in the transformation by which a substituted isothiohydantoin furnishes a substituted 'dioxythiazole,' the nitrogen member of the parent ring is exchanged for an oxygen atom, thus:

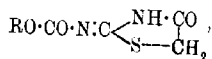


whence it follows that the foregoing carboalkyloxyisothiohydantoin has the constitution represented by formula II.

Judgment in the case of mono-substitution derivatives is a less simple matter. Analogy would suggest the formula



which also is consistent with the fact that, on hydrolysis by acid, they rapidly yield carbon dioxide, ammonia, and dioxythiazole. Moreover, that the latter does not result through the hydrolysis of isothiohydantoin, possibly formed from a compound,



is clear; because, whilst the actual hydrolysis is speedily accomplished, that of isothiohydantoin, in like circumstances, is very slow, yet the presence of this compound could not be detected in the mixture. Nevertheless, it is conceivable that a substituted

dioxythiazole,  $\text{CO}_2\text{R}\cdot\text{N}:\text{C} < \begin{array}{c} \text{O}\cdot\text{CO} \\ | \\ \text{S} - \text{CH}_2 \end{array}$ , might be formed and then hydrolysed, with elimination of the group  $\cdot\text{CO}_2\text{R}$ . Substances of the class last formulated are unknown.

Through the action of chloroacetyl chloride on  $\alpha$ -acetyl- $\beta$ -carboethoxythiocarbamide it should be possible to synthesise a compound having the structure  $\text{CO}_2\text{Et}\cdot\text{N}:\text{C} < \begin{array}{c} \text{NH}\cdot\text{CO} \\ | \\ \text{S} - \text{CH}_2 \end{array}$ , and if this should

prove isomeric with that from carbethoxythiocarbamide itself, decision would be easy. In practice, however, such a check could not be applied, all attempts to produce a thiocarbamide of the required configuration being unsuccessful.

## EXPERIMENTAL.

### *Phenylcarbethoxyisothiohydantoin.*

When *ab*-phenylcarbethoxythiocarbamide was heated on the steam-bath with slightly more than one molecular proportion of chloroacetyl chloride, liquefaction occurred with disengagement of hydrogen chloride and rapid deposition of a brown solid, the action being complete within a few minutes.

By recrystallisation from hot glacial acetic acid, which dissolves it freely, the product was obtained in white needles, sparingly soluble in boiling alcohol, benzene, acetone, or cold acetic acid, and commencing to decompose at about 220°, but melting only towards 250°. The substance is very slowly desulphurised by boiling with the alkaline solution of a lead salt, but readily yields silver sulphide when heated with ammoniacal silver nitrate. That it contains the group  $\text{-S-CH}_2\text{-CO-}$  was shown by boiling the substance with alcoholic potassium hydroxide, acidifying the liquor, and mixing with ferric chloride, followed by ammonia, the resultant purple coloration indicating (Andreaseh, *Ber.*, 1879, **12**, 1385) the presence of  $\alpha$ -thiolacetic acid.

Found: N=10·58; S=12·2.

$\text{C}_{12}\text{H}_{12}\text{O}_3\text{N}_2\text{S}$  requires N=10·60; S=12·12 per cent.

A mixture of ethyl chloroacetate and *ab*-phenylcarbethoxythiocarbamide, in alcoholic solution, was boiled for three hours under reflux with excess of calcium carbonate, and filtered whilst hot. From the filtrate, as it cooled, the unchanged thiocarbamide separated in crystals, and the mother liquor gave no reaction for  $\alpha$ -thiolacetic acid; in these circumstances, therefore, neither an *iso*-thiohydantoin nor an *isothio*hydantoic acid had been formed.

*Hydrolysis.*—Hot concentrated hydrochloric acid rapidly dissolved the substance, carbon dioxide being evolved, and from the solution as it cooled, 'phenyldioxythiazole' separated in long, flattened prisms melting at 143–144°. In different experiments the yield varied from 60 to 80 per cent. of the theoretical.

The acid liquor from which the crystals had been deposited gave on evaporation, ammonium chloride together with a little aniline hydrochloride. As phenyldioxythiazole itself yielded no aniline when heated with hydrochloric acid, it is possible that the *isothio*

hydantoin,  $\text{PhN}:\text{C} \begin{array}{l} \text{N}(\text{CO}_2\text{Et})\cdot\text{CO} \\ \text{S} \quad \text{CH}_2 \end{array}$ , contained a trace of the isomeride,  $\text{CO}_2\text{Et}\cdot\text{N}:\text{C} \begin{array}{l} \text{NPh}\cdot\text{CO} \\ \text{S} \quad \text{CH}_2 \end{array}$ , from which aniline would be producible.

*Phenylcarbomethoxyisothiohydantoin.*

This was prepared in the manner already described, but from  $\alpha$ -phenyl-*b*-carbomethoxythiocarbamide, and was similarly recrystallised from acetic acid. Marked decomposition occurred during the preparation, and the yield was poor. Except that the compound was rather more readily soluble in cold acetic acid, it resembled alike in properties and in reactions the carbethoxy-homologue; when heated, it decomposed gradually, but did not melt, even at  $250^\circ$ .

Found: S=12.45.

$\text{C}_{11}\text{H}_{10}\text{O}_3\text{N}_2\text{S}$  requires S=12.8 per cent.

*Phenylcarboxy-o-tolyliothiohydantoin.*

$\alpha$ -Phenyl-*b*-carboxy-*o*-tolylthiocarbamide (7.6 grams), in dry benzene, was heated for three hours, under reflux, with excess of chloroacetyl chloride. On cooling, crystals were deposited which, after recrystallisation from alcohol, weighed 1.3 grams, the original mother liquor, when evaporated, giving 3.5 grams of unchanged thiocarbamide; the yield, therefore, was but 28 per cent. of the theoretical.

Found: N=8.42; S=9.85.

$\text{C}_{17}\text{H}_{14}\text{O}_3\text{N}_2\text{S}$  requires N=8.59; S=9.82 per cent.

The substance occurred in white, rectangular prisms, sparingly soluble in cold alcohol or benzene, and melting at  $169$ – $170^\circ$ . Desulphurisation by boiling with the alkaline solution of a lead salt was slow and imperfect, even on prolonged boiling; but, with hot ammoniacal silver nitrate, blackening took place readily. By hot alcoholic potassium hydroxide  $\alpha$ -thiolacetic acid was produced, and recognised by Andreasch's method; owing, however, to lack of material, no further experiments could be made towards deciding the constitution of the substance.

The original thiocarbamide, when boiled with ethyl chloroacetate and alcohol in the presence of calcium carbonate, afforded not a trace of the above isothiohydantoin.



*Carbethoxyisothiohydantoin.*

Carbethoxythiocarbamide and chloroacetyl chloride were heated with benzene under reflux until hydrogen chloride ceased to escape, the action being complete in about three hours. During the process a yellow solid was deposited, consisting of the impure hydrochloride of the above base, which latter was obtained by dissolving the product in hot acetic acid, filtering off any hydrochloride that separated on cooling, and evaporating the filtrate in a vacuum. More readily, it is obtainable from the crude hydrochloride by recrystallisation from alcohol, mixed with finely divided calcium carbonate.

When ethyl chloroacetate was used, instead of chloroacetyl chloride, no sign of interaction was detectable after three hours' boiling; but when the experiment was repeated with an alcoholic solution in the presence of calcium carbonate, this being filtered off at the end of one and a-half hours, the filtrate, on cooling, deposited the nearly pure base.

*Carbethoxyisothiohydantoin* separates from alcohol in white, hard, felted needles, melting and decomposing at  $173-174^{\circ}$ ; it is sparingly soluble in cold water, moderately soluble in methyl alcohol, more readily so in ethyl alcohol, and dissolves freely in glacial acetic acid. It is not desulphurised by boiling with the alkaline solution of a lead salt or with ammoniacal silver nitrate, but is hydrolysed by hot alcoholic potassium hydroxide, with the formation of  $\alpha$ -thiolacetic acid.

Found: N=14.84; S=17.11.

$C_6H_8O_3N_2S$  requires N=14.90; S=17.02 per cent.

Hot dilute hydrochloric acid readily dissolved the substance, with effervescence due to the escape of carbon dioxide, and from the solution, when it had been evaporated down to a small bulk, crystals were deposited melting at  $120-125^{\circ}$  and consisting of nearly pure dioxithiazole.

The *hydrochloride* formed cream-white needles, commencing to decompose at about  $160^{\circ}$ , but not melting at  $200^{\circ}$ . Insoluble in benzene, it dissolves in hot acetic acid with the loss of part, but not all, of the combined hydrogen chloride. By dissolution in hot water it is rapidly and completely decomposed, the liberated acid converting the base into dioxithiazole; with boiling alcohol the same change occurs, but more slowly.

Found: S=14.62.

$C_6H_8O_3N_2S.HCl$  requires 14.25 per cent.

*Carbomethoxyisothiohydantoin.*

From carbomethoxythiocarbamide, in benzene, and chloroacetyl chloride the hydrochloride was obtained as in the last preparation, and on recrystallisation from acetic acid gave the pure base. Similarly, from the above thiocarbamide and ethyl chloroacetate in the presence of calcium carbonate (but not in its absence) the free base was obtained.

In respect of general properties and reactions, carbomethoxyisothiohydantoin closely resembles the carbethoxy-homologue, being, however, somewhat less readily soluble in methyl alcohol, ethyl alcohol, or glacial acetic acid. It has no definite melting point, but decomposes from about 170° onwards, being still unmelted at 220°.

Found: N=16·05; S=18·24.

$C_5H_6O_3N_2S$  requires N=16·09 S=18·39 per cent.

On contact with hot dilute hydrochloric acid, it dissolved with escape of carbon dioxide, the solution, when evaporated, giving ammonium chloride, together with dioxythiazole. (Found, S=26·85; dioxythiazole requires S=27·35 per cent.)

By alkaline hydrolysis it yielded  $\alpha$ -thiolacetic acid, which was recognised as before.

*Carbophenoxyisothiohydantoin.*

Carbophenoxythiocarbamide in dry benzene, when heated under reflux with chloroacetyl chloride, gave a yellow, crystalline mass of the substituted isothiohydantoin hydrochloride. By treatment with boiling alcohol containing finely divided calcium carbonate in suspension, the free base was obtained in faintly yellow crystals melting at 185–186°.

Found: S=13·51.

$C_{10}H_8O_3N_2S$  requires S=13·56 per cent.

Hydrolysis with hot alcoholic potassium hydroxide gave a solution responding to Andreasch's test for  $\alpha$ -thiolacetic acid.

With the foregoing thiocarbamide, in alcohol, ethyl chloroacetate failed to react, even in the presence of calcium carbonate—a result differing sharply from that observed with the carbethoxy- or with the carbomethoxy-analogue. The experiment was repeated, carbocetyloxythiocarbamide being used instead, but in this case, too, no interaction took place.

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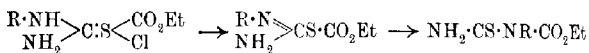
## XII.—Carboalkyloxythiocarbamides.

By AUGUSTUS EDWARD DIXON and RAYMOND THOMAS JOACHIM  
KENNEDY.

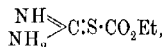
IN the course of a recent investigation (see preceding paper), progress was much retarded through the difficulty experienced in preparing sufficient quantities of certain necessary thiocarbamides, particularly those containing the carbomethoxy- or the carbethoxy-group, alone. Although such compounds are known, having been obtained both from the corresponding thiocarbimides and ammonia (Doran, T., 1896, **69**, 331) and by the hydrolysis of aldehyde-ammonia derivatives of the former (Dixon and Taylor, T., 1916, **109**, 1260), the yields are far from satisfactory—at all events, the best yield now attained by either method did not exceed 5 per cent. of the theoretical.

From *ab*-acetylphenylthiocarbamide, by heating it with excess of ethyl chlorocarbonate, the acetyl radicle is expelled as chloride, with the formation of the corresponding *ab*-carbethoxyphenylthiocarbamide (Doran, T., 1901, **79**, 913); it seemed, therefore, almost a foregone conclusion that from acetylthiocarbamide, in like circumstances, the products must be acetyl chloride and carbethoxythiocarbamide,  $\text{NH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ . This forecast proved incorrect, for, on experiment, no trace of the latter substance was obtained.

By treating with dilute alkali hydroxide the additive compound of a hydrocarbon mono-substituted thiocarbamide and a chlorocarbonate, Dixon succeeded in realising the changes



on the other hand, the corresponding, non-substituted base,

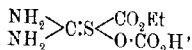


when similarly liberated from its 'hydrochloride,' broke down without yielding carbethoxythiocarbamide (T., 1903, **83**, 558, 565).

In the last case, the attack of the alkali hydroxide being primarily on the carbethoxy-group, it seemed probable that if alkali bicarbonate were used instead of alkali hydroxide, the disruption of that group might at least be hindered for a while. If so—the speed of migration of an acyl radicle from sulphur to nitrogen being often a matter of seconds—even a slight delay in the breaking down of the carbethoxy-complex might leave time enough for its transference.

Experimentally, this prevision has been justified by the production of the compounds sought, namely, carbomethoxy- and carbethoxy-thiocarbamides; they have been obtained, however, only indirectly, and through some unexpected intermediate reactions. Briefly, the facts are as follows.

Thiocarbamide-ethyl chlorocarbonate,  $\text{NH}_2\text{C}(\text{NH}_2)\text{S}(\text{Cl})\text{CO}_2\text{Et}$ , in aqueous solution yields with sodium hydrogen carbonate a bulky, white precipitate of the corresponding bicarbonate,



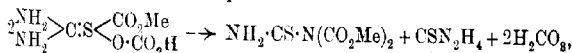
an unstable compound, which soon changes into a compact mass of prisms consisting of *aa*-dicarbethoxythiocarbamide; concurrently, thiocarbamide is liberated and passes into solution, along with the sodium chloride. The dicarbethoxythiocarbamide, itself stable, is readily hydrolysed in alcoholic solution by hydrochloric acid, with the formation of the monocarbethoxy-derivative,



Although the bicarbonate soon decomposes, especially in the presence of water, the change requires a certain time, and the bulky precipitate, if treated at once with dilute hydrochloric acid, dissolves, thereby furnishing a clear solution of the original salt (thiocarbamide-ethyl chlorocarbonate, in aqueous solution, gives a pierate identical with that obtained from the above solution of the bicarbonate in acid). The bicarbonate, after some twenty-four hours' keeping in a desiccator, changed completely into a mixture of thiourea and dicarbethoxythiocarbamide.

Thiocarbamide-methyl chlorocarbonate behaves similarly.

The spontaneous change of a salt containing but one carbethoxy- (or carbomethoxy-) group into an *aa*-di-substituted thiocarbamide is a remarkable phenomenon. That the last-named substance really has the *aa*-configuration follows from experimental results, that will presently be stated; moreover, that it is no mere by-product is clear, for, reckoned on the weight of 'hydrochloride' employed and calculated from the equation

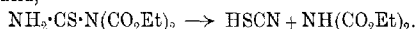


the yield of di-substitution derivative may reach at least 70 per cent. of the theoretical.

As regards the migration of an acyl group from sulphur to nitrogen, the process is of a kind now well established as normal. Further, if one of the two nitrogen atoms of the acyl- $\psi$ -thiocarbamide is charged already with a hydrocarbon radicle, the wander-

ing acyl group goes always to join the latter (see, for example, Dixon and Hawthorne, T., 1907, **91**, 128), and may either remain there permanently, or may again move, spontaneously or under stress, to the other; but, to the already substituted nitrogen atom, it goes in the first instance. Consequently, if the group  $\cdot\text{CO}_2\text{R}$  has made its normal excursion to yield the substituted thiocarbamide,  $\text{NH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{CO}_2\text{R}$ , it seems natural that a second, following in after the first, should take up the same station, at all events temporarily. In the case here considered, one may reasonably suppose that the second radicle is furnished by another molecule of the base,  $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{S}\cdot\text{CO}_2\text{R}$ , which holds it only loosely; and the fact that thiourea, not initially present, is found eventually along with the di-substitution product, is consistent with such a view. Still, it is a curious change, and all attempts hitherto made to reproduce it with other acyl sulphonium salts have proved unsuccessful.

For the structure,  $\text{NH}_2\cdot\text{CS}\cdot\text{N}(\text{CO}_2\text{R})_2$ , assigned to the foregoing dicarboalkyloxythiocarbamides, the experimental evidence is that the dicarbethoxy-compound, by cold concentrated alkali hydroxide, is resolved into thiocyanic acid and the ethyl ester of iminodicarbonic acid,

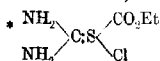


Those *aa*-derivatives are white. According to E. A. Werner (T., 1916, **109**, 1124), the yellow diacetylthiourea, obtained from acetic anhydride and thiourea in the presence of a mineral acid, is a  $\psi$ -thiocarbamide,  $\text{MeCO}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{S}\cdot\text{COMe}$ . Whether this really expresses the constitution of the compound, it is somewhat difficult to judge from the evidence adduced, since part of the latter—notably the decomposition, by heat, into acetamide and acetylthiocarbimide—would equally well support the *ab*-formula. In the present connexion, however, the sole point of interest was to learn whether the two acyl radicles might possibly be attached to the same nitrogen atom. On treatment with concentrated alkali hydroxide, however, the diacetyl compound afforded not a trace of thiocyanic acid, a result decisive against that view.

#### EXPERIMENTAL.

##### *Carbethoxy-derivatives.*

To a concentrated aqueous solution of thiocarbamide-ethyl chlorocarbonate,\* sodium hydrogen carbonate was added in slight



. This name is not quite so cumbrous as diamino-methylenecarbethoxysulphonium chloride. Besides, it is not impossible that the compound may be an ammonium salt.

excess; carbon dioxide was rapidly evolved, a crystalline material being deposited, which, after it had remained for some time, was collected, washed, and dried. The product formed shining, white, rectangular plates melting at  $97^{\circ}$  with effervescence, and with the evolution of carbethoxythiocarbimide, easily recognised by its characteristic odour. Practically insoluble in water or in benzene, it dissolved freely in alcohol, the solution giving with ammoniacal silver nitrate a black precipitate of silver sulphide, but resisting desulphurisation by the alkaline solution of a lead salt, even after prolonged boiling. Analysis showed the compound to be a dicarbethoxythiocarbamide.

Found: N=12.64; S=14.44.

$C_7H_{12}O_4N_2S$  requires N=12.73; S=14.54 per cent.

In cold concentrated alkali hydroxide, the substance dissolved readily, a portion of the liquid, when acidified and then treated with ferric chloride, giving the reaction of thiocyanic acid. From the remainder, ether extracted a material having the properties and giving the reactions of diethyl iminodicarbonate (Found: N=8.68.  $C_6H_{11}O_4N$  requires N=8.69 per cent.).

When allowed to evaporate spontaneously, the liquor from which the dicarbethoxythiocarbamide had separated left a residue of sodium chloride mixed with thiourea.

Dicarbethoxythiocarbamide is practically insoluble in dilute hydrochloric acid. Yet the precipitate obtained by means of sodium hydrogen carbonate, if treated immediately with a dilute acid, dissolved at once, and the solution gave with picric acid a sparingly soluble, bright yellow *picrate* melting at  $150-151^{\circ}$ . From an aqueous solution of thiocarbamide-ethyl chlorocarbonate, a *picrate* was obtained having the same melting point, and a mixture of the two, in equal proportions, melted also at  $150-151^{\circ}$ ; evidently, the bicarbonate precipitate, when freshly prepared, is transformable into the salt from which it was generated.

That precipitate, originally voluminous, but shrinking as it changes into the thiocarbamide, was supposed at first to be the free base, carbethoxy- $\psi$ -thiocarbamide,  $NH_2 \cdot C(NH) \cdot S \cdot CO_2Et$ . Strange to say, this is not so; it is an unstable salt, apparently the bicarbonate of the base. When filtered off as rapidly as possible, washed with acetone, and dried in bibulous paper, it formed rectangular plates, melting and effervescing at  $59-60^{\circ}$ , having a distinct odour of carbethoxythiocarbimide, and dissolving in acid with the evolution of carbon dioxide to a clear solution; in plain water it dissolved appreciably, but without effervescence.

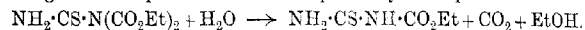
Found: N=15.2; S=16.4.

$C_5H_{10}O_3N_2S$  requires N=15.64; S=17.87 per cent.

Naturally, the experimental figures are no more than roughly approximate to those calculated. After twenty-four hours' keeping in a vacuum desiccator, the substance had completely decomposed into a mixture (m. p. 70—100°), from which water extracted a portion, leaving a residue of slightly impure dicarbethoxythiocarbamide. The aqueous extract, when treated with hydrochloric acid and potassium nitrite, followed by picric acid, yielded the picrate of formamidine disulphide, recognised by its melting point and by the mixed melting-point method; hence it contained thiourea. Neither carbethoxythiocarbamide nor *aa*-dicarbethoxythiocarbamide yields a derivative of formamidine disulphide under the above conditions, nor does either of them give a picrate with aqueous picric acid.

Further to confirm that the unstable substance is a carbonate (and not the corresponding free base), a quantity of the freshly prepared material, in aqueous solution, was mixed with a clear solution of basic lead acetate, whereon lead carbonate was precipitated. To the filtrate, freed from most of the lead by means of hydrochloric acid, and subsequent filtration, picric acid was added, the picrate of carbethoxy- $\psi$ -thiocarbamide (see above) thus being obtained.

Carbethoxythiocarbamide is formed when a solution of *aa*-dicarbethoxythiocarbamide, in alcohol, is acidified with hydrochloric acid; on keeping, the former gradually separates in crystals, the yield being about 80 per cent. of that required by the equation



More easily, it may be obtained by adding excess of sodium hydrogen carbonate to an alcoholic solution of thiocarbamide-ethyl chlorocarbonate, and shaking the mixture from time to time; when the reaction is at an end, the turbid mixture is filtered, the filtrate being then acidified and set aside for the crystals to separate. Although, in relation to the amounts of thiocarbamide and of ethyl chlorocarbonate originally taken, the yield is not very gratifying, yet, compared with that of the methods earlier mentioned, it is highly productive; the process, too, is facile of operation, because the 'hydrochloride' may be obtained by passing carbonyl chloride through a suspension of thiourea in benzene and absolute alcohol (compare T., 1903, **83**, 565).

#### *Carbomethoxy-derivatives.*

Thiocarbamide-methyl chlorocarbonate, in aqueous solution, gave with sodium hydrogen carbonate a bulky, white precipitate, melting at 62.5—63.5°, and resembling in general properties the carbethoxy-homologue, except for a slightly greater solubility in water. The

freshly prepared hydrogen carbonate,  $\text{NH}_2\text{C}(\text{NH}_2)\text{S}(\text{CO}_2\text{Me})$  dissolved readily and completely in cold dilute hydrochloric acid, the solution yielding with picric acid a sparingly soluble, bright yellow *picrate* melting at  $207-210^\circ$ .

Found: N=14.72; S=17.44.

$\text{C}_4\text{H}_8\text{O}_5\text{N}_2\text{S}$  requires N=14.28; S=16.33 per cent.

To measure the carbon dioxide, a portion was treated in the Lunge nitrometer, over mercury, with excess of dilute hydrochloric acid.

Found:  $\text{CO}_2=21.65$ . Theory requires  $\text{CO}_2=22.45$  per cent.

Decomposition was slower than in the case of the carbethoxy-derivative, the solid, even after twenty-four hours' keeping, still effervescing slightly on acidification; at the end of two days, however, the change was complete. By means of cold water, the thiourea was extracted, a mass of white, rhombic plates being left; they were readily soluble in alcohol, but practically insoluble in water, ether, acetone, benzene, or light petroleum, and melted at  $117-118^\circ$ .

Found: N=14.44; S=16.54.

$\text{C}_5\text{H}_8\text{O}_4\text{N}_2\text{S}$  requires N=14.58; S=16.67 per cent.

Reckoned from the weight of thiocarbamide-methyl chlorocarbonate employed, the yield of dicarbomethoxythiocarbamide was about 70 per cent. of the theoretical.

In cold concentrated alkali hydroxide, the substance dissolved at once, the solution reacting copiously for thiocyanic acid; hence both carbomethoxy-groups are attached to the same nitrogen atom.

The alcoholic solution, when acidified with hydrochloric acid, gradually deposited crystals of carbomethoxythiocarbamide. In this case, however, as in that of the higher homologue, it is unnecessary to prepare the *aa*-compound; an alcoholic solution of thiocarbamide-methyl chlorocarbonate (which may be prepared from thiourea in methyl alcohol-benzene suspension and carbonyl chloride), when treated with sodium hydrogen carbonate and then acidified, gives the mono-substitution derivative in yield varying from 60 to 70 per cent. of the theoretical.

A solution of thiocarbamide-methyl chlorocarbonate in water remained practically clear after some weeks' keeping, and hence had developed neither carbomethoxy- nor dicarbomethoxy-thiocarbamide. Decomposition slowly occurred, partly with regeneration of thiourea and partly with the formation of the hydrochloride of methyl- $\psi$ -thiocarbamide,  $\text{NH}_2\text{C}(\text{NH})\text{SMe}$ .

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### XIII.—Organic Derivatives of Tellurium. Part I. Dimethyltelluronium Dihaloids.

By RICHARD HENRY VERNON.

THE first mention of dimethyltelluronium di-iodide,  $\text{TeMe}_2\text{I}_2$ , is by Demarçay (*Bull. Soc. chim.*, 1883, [ii], 40, 99), who merely states that this substance is obtained by the action of methyl iodide on tellurium, and that decomposition takes place at  $100\text{--}120^\circ$ .

In 1904, Scott (P., 1904, 20, 157) confirmed Demarçay's work, mentioned that neither sulphur nor selenium behaves in a similar manner, and described the preparation of trimethyltelluronium iodide.

The present paper is more in the nature of an introduction to the chemistry of this singular di-iodide, and its main object is to show that there are not only two dimethyltelluronium di-iodides, two dibromides, and two dichlorides, but that these haloid derivatives of the bivalent radicle "dimethyltelluride" are respectively isomeric.

The reason for this duplication is that there are two bases, and that each base gives a corresponding series of derivatives.

The first, or  $\alpha$ -base, is obtained by treating Demarçay's red iodide with silver oxide and water. An aqueous solution with markedly basic properties results.

To prepare the second, or  $\beta$ -base, the solution of the  $\alpha$ -base is evaporated to dryness under specified conditions, and the white, crystalline mass redissolved in water.

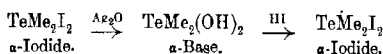
The chemical behaviour towards reagents of these two bases is shown in the following table, the solutions in each case being precisely of the same concentration.

Reagent	Aqueous solution of $\alpha$ -base.	Aqueous solution of $\beta$ -base.
$\text{AgNO}_3$ .....	Precipitate of $\text{Ag}_2\text{O}$ .	White precipitate. Becomes black on boiling.
$\text{FeCl}_3$ .....	Precipitate of $\text{Fe(OH)}_3$ when base is in excess.	White precipitate when base is in excess.
$\text{FeCl}_3$ .....	A red solution becoming darker on boiling.	No precipitate when $\text{FeCl}_3$ is in excess.
$\text{H}_2\text{PtCl}_6$ .....	No precipitate.	Yellow platinum salt.
Picric acid .....	No precipitate.	Yellow picrate.

The best reaction to distinguish between them is that with silver nitrate, and this first directed the author's attention to their existence. Another typical reaction is with ferric chloride. Both these bases form picrates, but that of the  $\alpha$ -base possesses a much greater solubility than that derived from the  $\beta$ -base. Generally speaking, the two bases behave towards metallic salts like the alkalis, the precipitates being apparently similar in some cases, but showing marked differences in others.

Apart from these reactions, the chief feature of interest lies in the action of the halogen acids.

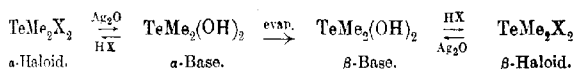
Thus, if the  $\alpha$ -base is treated with hydriodic acid, the original  $\alpha$ -iodide, namely, Demarçay's, is regenerated.



On treatment of the  $\beta$ -base with hydriodic acid, in marked contrast to the  $\alpha$ -, Demarçay's iodide is not regenerated, but a new iodide totally different in chemical and physical properties, and this new or  $\beta$ -iodide has proved to be isomeric with the  $\alpha$ - or Demarçay's iodide. The equation now becomes:



Repeated attempts have so far shown that, although the  $\alpha$ -base easily changes into the  $\beta$ -, the reverse is not the case. Furthermore, each iodide is converted into its corresponding base on treatment with silver oxide, and hence the still more generalised equation can be written:



where X is either chlorine, bromine, or iodine, precisely the same reactions taking place with the other two halogen acids as with hydriodic acid itself.

There are thus six dimethyltelluronium dihaloids of the general type  $\text{TeMe}_3\text{X}_2$ , and in future all derivatives of the  $\alpha$ -base will be prefixed by the letter  $\alpha$  and those of the  $\beta$ -base by the letter  $\beta$ .

This is very necessary, because not only do the two haloid series exist, but every salt is duplicated. This does not imply, however, that they are necessarily isomeric.

*Melting Points.*—The following is a comparison of the melting points:

$\alpha$ -Chloride : 92°	$\beta$ -Chloride : 134°
$\alpha$ -Bromide : 92°	$\beta$ -Bromide : 142°
$\alpha$ -Iodide : 127°	$\beta$ -Iodide : (no m. p.)

Of these, the  $\alpha$ -chloride and bromide melt sharply without decomposition, and the remainder decompose on fusion. The  $\beta$ -iodide imperceptibly changes into tellurium and methyl iodide above  $100^{\circ}$ , but no sign of fusion is observed.

*Colour and Absorption Spectra.*—Solutions of the dimethyl-telluronium dihaloids have somewhat different colours from the salts themselves, and this is particularly marked with the two iodides.

The bright red crystals of the  $\alpha$ -iodide give a deep orange solution, and the black or greenish-black crystals of the  $\beta$ -iodide a blood-red one. The following table gives the colour of the salts and their solutions:

	Salt.	Solution (N/100 in ethyl alcohol).
$\alpha$ -Chloride .....	Colourless.	Colourless.
$\beta$ -Chloride .....	Tinged.	Tinged.
$\alpha$ -Bromide .....	Yellowish.	Yellowish.
$\beta$ -Bromide .....	Orange	Orange.
$\alpha$ -Iodide .....	Red.	Deep orange.
$\beta$ -Iodide .....	Black (greenish- black).	Blood-red.

Of considerable interest is the absorption spectra in the ultra-violet region, photographs of which were obtained through the

Salt.	Thickness of solution.	$\lambda$
$\alpha$ -Chloride .....	2 mm.	2640
	10 "	2742
	20 "	2760
	30 "	2780
$\beta$ -Chloride .....	2 mm.	2680
	10 "	2750
	20 "	2890
	30 "	2935
$\alpha$ -Bromide .....	2 mm.	3005
	10 "	3245
	20 "	3300
	30 "	3350
$\beta$ -Bromide .....	2 mm.	3045
	10 "	3310
	20 "	3405
	30 "	3450
$\alpha$ -Iodide .....	2 mm.	3940
	10 "	4190
	20 "	4320
	30 "	4425
$\beta$ -Iodide .....	2 mm.	4350
	4 "	4425

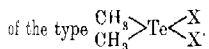
kindness of Mr. J. E. Purvis. Hundredth-mol. solutions, in ethyl alcohol, were used in each case, and fifteen photographs were taken on each plate. The source of illumination was a cadmium spark, and the exposure was two minutes for each photograph. In no case were any bands observed, and the positions where general absorption began are given for thicknesses of 2, 10, 20, and 30 mm.

It will be noticed that (1) the  $\beta$ -haloid has a greater absorbing power than the corresponding  $\alpha$ -one, and (2) the  $\alpha$ -chloride shows the least absorption and the  $\beta$ -iodide the greatest, the latter absorbing to the extent of complete extinction through a thickness of solution greater than 4 mm.

In view of the enormous absorbing power of the two iodides, and especially of the  $\beta$ -iodide, two extra spectrographs were taken using a ten-thousandth-mole solution (ethyl alcohol), otherwise precisely the same conditions were maintained, and although a marked difference between the two was still noticeable, no bands were apparent.

*Constitution.*—(1) The existence of two series of dimethyl-tellurium dihaloids has been established. In the case of each of the chlorides, bromides, and iodides it has been shown\* (i) that they have the same percentage composition, (ii) that they have the same molecular weight, and (iii) that there is no question of polymorphism, since (a) the absorption spectra are different, and (b) their chemical behaviour is different, thus each regenerates its respective base when treated with silver oxide. The conclusion is, therefore, that these haloids must be respectively isomeric.

(2) Since in the  $\alpha$ - as well as in the  $\beta$ -series both halogens are ionisable, the halogen being precipitated quantitatively by silver nitrate, and both the  $\alpha$ - and the  $\beta$ -bases are strongly diacidic, the haloids of both series must be represented by structural formulae



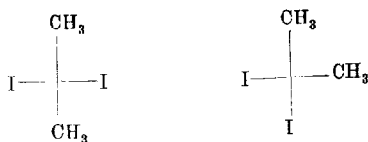
(3) The fact that there exist in these simple compounds of quadrivalent tellurium two substances corresponding with one structural formula shows that the relationship between the four tellurium valencies must be different from that generally assumed to exist between the carbon valencies in such a compound as methylene iodide, that is, there cannot be four equal valencies directed towards the solid angles of a regular tetrahedron of which the tellurium atom occupies the centre.

\* Analytical figures and molecular weights will be found in the experimental part.

(a) The four tellurium valencies might have different values and not be equivalent to one another.



(b) Their arrangement might differ widely from the regular tetrahedral disposition. The most symmetrical disposition that would account for the existence of the two isomerides would be that in which the four valencies are in one plane.



(c) Another suggestion that might be put forward is that the tellurium atom occupies the apex of a pyramid with a rectangular base.

(4) The discussion of the exact cause of the isomerism will be fully dealt with in a later paper. The purpose of the present communication is merely to show that the compounds  $\text{TeMe}_2\text{X}_2$  actually exist in two isomeric forms.

#### EXPERIMENTAL.

##### *The α- or Demarçay's Iodide (α-Dimethyltelluronium Di-iodide).*

According to Demarçay, this substance is obtained directly by heating at  $80^\circ$  a mixture of methyl iodide and tellurium in the proportion of two mols. of the former to one of the latter.

The best method of procedure is to blow a 150—200 c.c. bulb on the end of a 1.5 to 2 cm. glass tube, seal up the contents (50 grams of amorphous tellurium and 112 grams of methyl iodide is a convenient amount), and keep in a water-bath at  $80^\circ$  for thirty-six to forty-eight hours. Very little pressure is developed at any time, and none will be found when the cold tube is opened. This is now broken into a mortar, the brittle, red mass finely powdered and extracted with chloroform, and if the same chloroform is used for repeated extractions, very little is necessary. A hot funnel will be required when filtering off the unchanged tellurium. The interaction between methyl iodide and tellurium is very rapid at first, but gradually becomes slow, and eventually appears to stop altogether, even on prolonged heating. In one experiment, when

50 grams of tellurium and 112 grams of methyl iodide were kept at 80° for forty-eight hours, a yield (the yields are calculated on the crystalline iodide obtained from chloroform) of 50 per cent. was obtained.

Precisely the same quantities, when kept at 80° for three weeks, gave only a 55 per cent. yield. The yields are proportionally greater when small quantities are used.

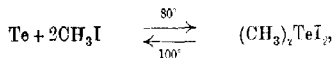
The  $\alpha$ -iodide crystallises from solvents in varying shades of red and melts and decomposes at 127°:

0.2293 gave 0.0490 CO<sub>2</sub> and 0.0325 H<sub>2</sub>O. C=5.83; H=1.57.

0.1890 in 34.65 benzene gave  $\Delta t = -0.068^\circ$ . M.W.=401.

C<sub>2</sub>H<sub>6</sub>I<sub>2</sub>Te requires C=5.83; H=1.46 per cent. M.W.=411.

The reaction between tellurium and methyl iodide is a reversible one,



proceeding from left to right at 80° and from right to left at or above 100°. In order to show this, a weighed quantity of the iodide was placed in a small bulb blown at the end of a 4 mm. tube, the open end being drawn out into a fine capillary tube and bent at right angles. This constituted a small distilling flask, and the iodide when carefully heated to 100° in a sulphuric acid bath began to decompose. The temperature was gradually raised to 180°, and the distillate collected in a weighed tube kept in ice:

1.2912 gave Te (residue)=0.4206; CH<sub>3</sub>I (distillate)=0.8352.

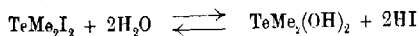
Te=32; CH<sub>3</sub>I=65.

C<sub>2</sub>H<sub>6</sub>I<sub>2</sub>Te requires Te=31; CH<sub>3</sub>I=69 per cent.

These figures are not in close agreement, but are sufficient to show that methyl iodide is the product of decomposition, and not dimethyl telluride. The distillate, also, was quite free from the overpowering odour of the telluride.

The  $\alpha$ -iodide is soluble in most organic solvents, the best being chloroform and benzene. To obtain good crystals, boiling saturated solutions should be allowed to cool, and, when cold, the solvent at once decanted, otherwise polymerisation sets in.

The  $\alpha$ -iodide is not soluble in cold water, but on prolonged boiling an orange-red solution is obtained which, on cooling, deposits the iodide, leaving a perfectly colourless solution. The salt is partly hydrolysed and the reaction is reversible.



A curious state of equilibrium between the  $\alpha$ -base and hydriodic acid results when a boiling saturated solution of the iodide is

suddenly poured into a large excess of cold water. A fine, yellow precipitate at once forms and as quickly disappears, the aqueous solution remaining quite colourless. The base is now in equilibrium with the hydriodic acid, and will remain so indefinitely.

If this perfectly colourless solution is evaporated, crystals of the iodide appear. If hydriodic acid is added, the iodide is at once precipitated.

The action of alkalis and of both aqueous and dry ammonia on the iodide will be dealt with in a separate paper.

A remarkable reaction, which is almost unique, is that between the iodide and mercury diphenyl. If boiling chloroform solutions of the two compounds are suddenly mixed, the mixture will remain perfectly clear and quiescent for a few seconds (this period depending on the concentration of the solutions and on the temperature, decreasing with an increase of concentration and inversely), and then, in a flash, the reaction sets in, and the perfectly clear solution instantly becomes opaque.

The explanation for this reaction probably lies in the formation of an oil (an excessively unstable form of the mercury compound), which is, moreover, very readily soluble in chloroform. At a given moment this oil suddenly changes into the more stable crystalline form, which is quite insoluble in chloroform. Experiment shows the existence of such an oil, and the complete insolubility of the crystalline mercury compound in chloroform rather confirms this hypothesis.

This mercury diphenyl reaction is very characteristic of the  $\alpha$ -iodide, and although similar compounds are formed with other aliphatic tellurium derivatives, such as with diethyltelluronium di-iodide (a lemon-yellow salt), the reaction does not take place in this curious manner.

Fuming or concentrated nitric acid precipitates the iodine from the  $\alpha$ -iodide, and if the mixture is evaporated on the water-bath the iodine is gradually expelled, and the colourless solution deposits white crystals of the  $\alpha$ -nitrate, which melts sharply and without decomposition at  $142^{\circ}$ . This nitrate is explosive when suddenly heated. The  $\alpha$ -iodide gives a green platinum salt with chloroplatinic acid.

#### *The $\alpha$ -Base.*

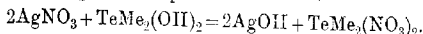
This is obtained from the  $\alpha$ -iodide by the action of silver hydride. Thirty-six grams of silver nitrate and 10 grams of sodium hydroxide are each dissolved in 500 c.c. of water, and the boiling solutions mixed. The mixture is vigorously boiled until the silver

hydroxide becomes granular, when it is collected and washed with 5 litres of boiling water.

Twenty-four grams of the iodide are now ground in a mortar with the freshly prepared silver hydroxide, and sufficient water to make a thin paste. When the red crystals have completely disappeared, the reaction is completed, but it is preferable to allow half an hour to elapse, with occasional grinding, before filtering. The reason of this is that a crystal of the iodide is very liable to become coated with silver iodide, thus impeding further action; hence thorough grinding is necessary.

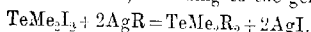
The silver iodide and mortar are now washed with boiling water, and the filtrate (150—200 c.c.), which is generally somewhat opalescent, contains the  $\alpha$ -base. The quantities indicated in this preparation allow for an excess of silver hydroxide.

This strongly alkaline solution behaves in a very similar manner to the mineral bases, and with silver nitrate gives silver hydroxide, probably according to the equation



With halogen acids, the  $\alpha$ -haloid series results, and undoubtedly a great number of  $\alpha$ -derivatives could be prepared with both mineral and organic acids.

The standard method of preparing these  $\alpha$ -salts is not by the action of the acid on the base, involving the preparation of the base from the iodide, but the direct interaction between the iodide and the silver salt of the acid, according to the general equation



In this manner, the *benzoate*, which crystallises in white needles melting at  $154^\circ$ , and the yellow *picrate*, crystallising in fine plates, were prepared.

#### The $\beta$ -Base.

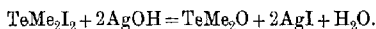
To prepare the  $\beta$ -base, the  $\alpha$ -base is evaporated at  $100^\circ$  under about 15 mm. pressure to complete dryness. The reaction can be closely followed by taking samples and testing with silver nitrate. The point at which the transition from the  $\alpha$ - to the  $\beta$ -base is just about to take place is reached when the violent ebullition ceases and an oily liquid remains in the evaporating flask. A sample of this oil, dissolved in water, still shows the presence of the  $\alpha$ -base with silver nitrate. If, however, the evaporation is continued for a few minutes longer, this oil, which has momentarily remained perfectly quiescent, will suddenly begin to bubble violently, apparently giving off water, and a white, leaf-like, crystalline substance which adheres to the side of the evaporating flask is obtained. This is the  $\beta$ -base. Due to the sparing solu-



bility of silver hydroxide in water, the base is invariably more or less coloured, the shade varying from pale to dark brown.

To obtain the colourless  $\beta$ -base, it is only necessary to redissolve the discoloured preparation in water, filter, and evaporate again to dryness. This operation can be repeated if necessary.

From 24 grams of the iodide, 6—7 grams of the base are usually obtained, this representing a yield of about 70 per cent. of the theoretical calculated from the equation



Owing to its extremely hygroscopic nature and the difficulty of thoroughly drying this base, a combustion gave but little information as to its constitution:

0.3488 gave 0.1610  $\text{CO}_2$  and 0.1041  $\text{H}_2\text{O}$ . C=12.58; H=3.31.

$\text{C}_2\text{H}_5\text{O}_2\text{Te}$  requires C=12.54; H=4.18.  $\text{C}_2\text{H}_6\text{OTe}$  requires

C=13.83; H=3.46 per cent.

As will be observed, the value obtained for carbon would indicate a dimethyltelluronium dihydroxide, but that obtained for hydrogen approaches more nearly to dimethyltelluronium oxide.

A certain amount of evidence tends to show that the  $\beta$ -base is dimethyltelluronium oxide, namely, its molecular weight in water, and analysis of the silver salt obtained by treating the base with silver nitrate:

0.5990 in 47.75 water gave  $\Delta^t = -0.143^\circ$ . M.W.=163. The hydroxide requires M.W.=192, and the oxide M.W.=173.\*

Analysis of the extremely unstable silver salt gave:

0.2814 gave 0.0403  $\text{CO}_2$  and 0.0305  $\text{H}_2\text{O}$ . C=3.91; H=1.20.

0.1952 „ 0.1088  $\text{AgCl}$ . Ag=41.95.†

$\text{C}_2\text{H}_6\text{OTe}, 2\text{AgNO}_3$  requires C=4.66; H=1.17; Ag=42.00 per cent.

These figures would therefore point to the existence of a dimethyltelluronium oxide, giving additive products with metallic salts, such as silver nitrate, ferric chloride, etc.

It would therefore not be surprising if similar additive compounds of the general type,  $\text{TeMe}_2\text{O}, 2\text{HX}$ , were formed with halogen acids, these constituting the  $\beta$ -series. Analysis alone is sufficient to refute this hypothesis.

Consideration of the analytical figures for the six haloids unquestionably shows that, whatever the constitution of the  $\beta$ -base may be, a salt results when it is treated with halogen acids, which must correspond in percentage composition and molecular weight

\* Two other values were 175 and 183.

† Other values for Ag were 41.90 and 42.00.

with the formula  $\text{TeMe}_2\text{X}_2$ , and in consequence the  $\beta$ -base must either have a similar constitution or at least a constitution that lends itself to the formation of such derivatives.

This base also possesses alkaline properties, has a powerful odour, is very hygroscopic, and is readily soluble in both water and alcohol.

With halogen acids, the  $\beta$ -series results, and probably a great number of  $\beta$ -salts, both of inorganic and organic acids, could be prepared.

As previously remarked, the transition from the  $\alpha$ - to the  $\beta$ -base readily occurs, but all attempts to obtain the reverse reaction have completely failed.

Prolonged boiling, as well as repeated evaporations to dryness, of an aqueous solution of the  $\beta$ -base, etc., have not produced the slightest change. That the  $\beta$ -form is the most stable of the two is unquestionably the case.

#### *The $\beta$ -Iodide ( $\beta$ -Dimethyltelluronium Di-iodide).*

This iodide is prepared by the action of hydriodic acid on the  $\beta$ -base. This, obtained as previously described from 24 grams of the  $\alpha$ -iodide, is dissolved in about 100 c.c. of water, and the acid (D 1.5) is run into it from a burette, the solution being contained in a mortar. A few c.c. are run in at first, and a black, viscid, tarry mass is at once formed which, on trituration, becomes very brittle, and can be finely powdered. This operation is repeated until further addition of hydriodic acid (about 17 c.c. are required) no longer produces a precipitate. This fine, purple powder, which is very heavy, settles rapidly, and the clear, supernatant liquid can be poured off. The crude iodide is collected and kept in a vacuum desiccator over calcium chloride and sodium hydroxide.

The dry salt is now dissolved in a minimum quantity of methyl alcohol, and the solution filtered through a hot funnel. The deep blood-red solution should immediately deposit crystals, and, when cold, these should be collected at once. The crystals can be recrystallised from methyl alcohol. It also appears to be advantageous to add one or two drops of hydriodic acid to the solvent. A point to be noted is that it is useless to evaporate mother liquors containing the  $\beta$ -iodide, as not only polymerisation, but partial decomposition, with precipitation of tellurium, takes place.

The crystals of the  $\beta$ -iodide vary somewhat in colour, being at times nearly black and at others of an iridescent green. The yields

are necessarily low, on account of loss during crystallisation, but 4 or 5 grams can usually be obtained:

0.8538 gave 0.1828  $\text{CO}_2$  and 0.1168  $\text{H}_2\text{O}$ . C=5.84; H=1.52.

0.3138 „ 0.3578  $\text{AgI}$ . I=61.62.

0.4482 in 32.55 acetone gave  $E=0.046^\circ$ . M.W.=509.

$\text{C}_2\text{H}_6\text{I}_2\text{Te}$  requires C=5.83; H=1.46; I=61.72 per cent.

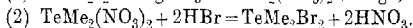
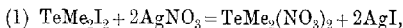
M.W.=411.\*

*The  $\alpha$ -Bromide ( $\alpha$ -Dimethyltelluronium Dibromide).*

The  $\alpha$ -bromide can be prepared by the action of hydrobromic acid on the  $\alpha$ -base. The solution of  $\alpha$ -base, prepared as described from 24 grams of the  $\alpha$ -iodide, usually has a volume of between 150 and 200 c.c., and should be evaporated to about 100 c.c. The acid (D 1.3) is now run in from a burette until no further precipitation takes place. The crude bromide is collected and crystallised from ethyl or methyl alcohol. A pure salt is at once obtained, and, after thoroughly drying over calcium chloride and sodium hydroxide, the leaf-like crystals melt at  $92^\circ$ . Unless the preparation is entirely freed from acid by drying over sodium hydroxide, the melting point will invariably be low.

A more direct method consists in dissolving the  $\alpha$ -iodide in aqueous ammonia, precipitating the iodine with an ammoniacal solution of silver nitrate, and treating the dimethyltelluronium dinitrate with hydrobromic acid.

This reaction is very complicated, but can be summarised by the equations:



Concentrated aqueous ammonia is run drop by drop from a burette on 15 grams of the  $\alpha$ -iodide (an exothermic reaction) until the red salt is completely transformed into a pasty, greyish-white mass. This will need but a few c.c., and it is advisable to stir thoroughly during the reaction, as the greyish-white precipitate has a tendency to cake, thus preventing further action of the ammonia. This precipitate is now dissolved in about 200 c.c. of water with a drop or two of ammonia if any of the undecomposed

\* Another determination gave M.W.=707. These values are high, owing to polymerisation of the salt in the solvent. Experiment has shown that: (1) the molecular weight increases regularly with the concentration, and (2) the molecular weight is higher in boiling acetone than it is in freezing nitrobenzene, for the same concentration. This polymerisation is more marked in the case of the  $\beta$ -iodide than it is with the  $\beta$ -bromide. The  $\beta$ -chloride shows no sign of polymerisation and correct values are obtained.

iodide is observed. Fifty c.c. of an aqueous solution containing 19.4 grams of silver nitrate, with just sufficient ammonia to redissolve the precipitate of silver hydroxide, are now added, and the mixture is boiled and filtered. The filtrate is evaporated on a water-bath until the odour of ammonia has completely disappeared, diluted again to 200 c.c., and any silver iodide removed by filtration.

A drop of hydrobromic acid is added to the boiling solution, and if a yellow, insoluble precipitate forms, this indicates an excess of silver nitrate. In this case, a further addition of acid is necessary. Any silver bromide is now filtered off, and the solution evaporated to about 100 c.c.

The cold filtrate is treated with acid (hydrochloric or hydrobromic, according as to whether the  $\alpha$ -chloride or  $\alpha$ -bromide is desired) until no further precipitation takes place. The crude salt can now be crystallised from ethyl or methyl alcohol. The yields are good, and about 5 or 6 grams are usually obtained after a second crystallisation from alcohol:

0.7248 gave 0.2004  $\text{CO}_2$  and 0.1246  $\text{H}_2\text{O}$ .  $\text{C}=7.54$ ;  $\text{H}=1.91$ .

0.3350 „ 0.3956 AgBr.  $\text{Br}=50.25$ .

0.6512 in 31.42 acetone gave  $E=0.105^\circ$ .  $\text{M.W.}=335$ .

$\text{C}_2\text{H}_6\text{Br}_2\text{Te}$  requires  $\text{C}=7.56$ ;  $\text{H}=1.89$ ;  $\text{Br}=50.39$  per cent.

$\text{M.W.}=317$ .

*The  $\beta$ -Bromide ( $\beta$ -Dimethyltelluronium Dibromide).*

The  $\beta$ -base from 24 grams of the  $\alpha$ -iodide is diluted to about 150 c.c., and hydrobromic acid (D 1.3) is run in from a burette (25–35 c.c. of acid are generally required).

So long as an excess of base is present, the white, gelatinous precipitate redissolves. On continued addition of acid, a somewhat granular, insoluble precipitate separates which, on further treatment, becomes bright orange and crystalline. This is the bromide, which can be recrystallised from ethyl alcohol, etc.

In this preparation, mother liquors containing a little free acid can be evaporated on a water-bath and allowed to crystallise.

A certain amount of tellurium, due to slight reduction, is liable to precipitate on treatment of the base with the acid, and this is especially the case when a too concentrated solution of the base is used. The crude bromide is therefore liable to be more or less discoloured.

It is also not advisable to have a marked excess of acid, as this appears to react further with the  $\beta$ -bromide, giving a brown,

additive compound. The yields are good, and 6 or 7 grams of the crude bromide can usually be obtained.

The leaf-like crystals, or bright orange, crystalline powder, darken at about  $135^{\circ}$  and melt and decompose at about  $142^{\circ}$ . Repeated crystallisations of this bromide do not alter the melting point:

0.6944 gave 0.1914  $\text{CO}_2$  and 0.1206  $\text{H}_2\text{O}$ .  $\text{C}=7.52$ ;  $\text{H}=1.93$ .

0.3564 „ 0.4218  $\text{AgBr}$ .  $\text{Br}=50.36$ .

0.3034 in 46.61 nitrobenzene gave  $\Delta t = -0.123^{\circ}$ .  $\text{M.W.}=370$ .

$\text{C}_2\text{H}_6\text{Br}_2\text{Te}$  requires  $\text{C}=7.56$ ;  $\text{H}=1.89$ ;  $\text{Br}=50.39$  per cent.

$\text{M.W.}=317$ .\*

*The  $\alpha$ -Chloride ( $\alpha$ -Dimethyltelluronium Dichloride).*

This is prepared in exactly the same manner as the  $\alpha$ -bromide, both by the action of hydrochloric acid on the base or directly from the  $\alpha$ -iodide. It is the most stable of all the dimethyltelluronium dihaloids, does not appreciably polymerise, and can be crystallised from water, alcohol, etc. From concentrated solutions leaf-like crystals deposit, and from dilute aqueous solutions long needles, with the same melting point of  $92^{\circ}$ , are obtained:

0.5693 gave 0.2196  $\text{CO}_2$  and 0.1340  $\text{H}_2\text{O}$ .  $\text{C}=10.52$ ;  $\text{H}=2.62$ .

0.3618 „ 0.4560  $\text{AgCl}$ .  $\text{Cl}=31.17$ .

0.2224 in 19.38 acetone gave  $E=0.085^{\circ}$ .  $\text{M.W.}=229$ .

$\text{C}_2\text{H}_6\text{Cl}_2\text{Te}$  requires  $\text{C}=10.50$ ;  $\text{H}=2.62$ ;  $\text{Cl}=31.05$  per cent.

$\text{M.W.}=228$ .

*The  $\beta$ -Chloride ( $\beta$ -Dimethyltelluronium Dichloride).*

To prepare this chloride, the directions given for the preparation of the  $\beta$ -bromide are followed. The precipitation of tellurium when hydrochloric acts on the base is not quite so marked as with the  $\beta$ -bromide, but the crude chloride is generally somewhat discoloured. The leaf-like crystals melt sharply at  $134^{\circ}$ :

0.3496 gave 0.1346  $\text{CO}_2$  and 0.0830  $\text{H}_2\text{O}$ .  $\text{C}=10.50$ ;  $\text{H}=2.64$ .

0.2206 „ 0.2777  $\text{AgCl}$ .  $\text{Cl}=31.11$ .

0.1648 in 19.11 acetone gave  $E=0.065^{\circ}$ .  $\text{M.W.}=226$ .†

$\text{C}_2\text{H}_6\text{Cl}_2\text{Te}$  requires  $\text{C}=10.50$ ;  $\text{H}=2.62$ ;  $\text{Cl}=31.05$  per cent.

$\text{M.W.}=228$ .

UNIVERSITY CHEMICAL LABORATORIES,  
CAMBRIDGE.

[Received, October 21st, 1919.]

\* Other values obtained for the molecular weight were: 400, 445 (nitrobenzene), 430, 459, 525 (acetone).

† Other values found were 230 : 223 (acetone).

#### XIV.—*The Action of Aqua Regia on Gold-Silver Alloys in the Presence of Ammonium Salts.*

By WILLIAM BRANCH POLLARD.

THE most practical method of dissolving gold and its alloys is undoubtedly by means of aqua regia.

With gold alloys containing upwards of 15 per cent. of silver, a coating of silver chloride forms on the surface of the metal and protects it from the further action of the acid.

By rolling out these alloys until they are very thin, solution can often be effected, the coating on the metal never becoming sufficiently thick to stop the reaction; thicker pieces are only superficially attacked.

With alloys which are very rich in silver, "rolling out" is not sufficient to effect solution, and a black coating forms and resists all further action of the acid.

In order to study the matter further, the following alloys were prepared, the composition being stated in parts per thousand:

Au.	Ag.	Cu.
625	375	—
500	500	—
333	667	—
250	750	—
453	277	270

The alloys were rolled out to about a tenth of a millimetre in thickness, and portions of them were used in the subsequent tests.

It seemed probable that the best way to effect solution of these alloys would be to try and increase the solubility of the silver chloride in the liquid; of the various chlorides which are known to dissolve silver chloride, ammonium chloride appeared to be the most promising for this purpose.

To test the point, a gram of each of the above-mentioned alloys was placed into a bottle, aqua regia (containing one part of concentrated nitric acid and three parts of concentrated hydrochloric acid) added, and the bottle placed on a hot asbestos board. The action of the acid started almost immediately, but stopped very quickly, the surface of the metal being covered with a black coating. Ammonium chloride was now added to the hot liquid as long as it was dissolved. In a very short time, the black coating on the metal had completely dissolved, leaving a bright, metallic surface in each case. The acid now began to attack the metal

again, and continued to do so until all had dissolved; no silver chloride separated, and a clear, yellow solution was obtained. On diluting the solutions with water, copious precipitates of perfectly white silver chloride separated. Even pure silver was found to be soluble in a mixture of aqua regia and ammonium chloride, although the action was not very rapid and the volume of liquid required was large in comparison with the amount of metal dissolved. It is to be noted that aqua fortis and sal-ammoniac were used by the alchemists for dissolving gold. It seems most probable that this mixture was used to dissolve native gold, which sometimes contains enough silver to prevent dissolution in aqua regia alone.

The chief objection to the use of aqua regia and ammonium chloride seemed to be that the action of the acid was very slow, and when much silver was present the volume of the solution became large.

It was noticed that the alloy containing gold 453, silver 277, and copper 270 dissolved very easily in a mixture of aqua regia and ammonium nitrate, the silver chloride remaining insoluble.

Alloys of gold and silver only did not dissolve so easily in this mixture, but when ammonium chloride was added as well, a most marked improvement took place.

For most alloys, a mixture of 5 grams of ammonium chloride, 5 grams of ammonium nitrate, and 5 to 10 c.c. of aqua regia was found to give quite satisfactory results.

The amount of metal which can be dissolved depends on the amount of silver present. If silver chloride separates, this shows that enough ammonium chloride has not been added. If, on the other hand, the action becomes slow, more aqua regia may be required.

With 5 grams of each salt and 5 to 10 c.c. of aqua regia, 0.5 to 1 gram of alloy could be dissolved easily and quickly, the total volume of the solution being quite small.

Considerably more gas is evolved when gold dissolves in the presence of ammonium salts than when it is dissolved in aqua regia alone; on collecting the gas, it appeared to consist principally of nitrogen. The solution of the gold, therefore, does not take place in accordance with Priwoznik's equation (*Oesterr. Zeitsch. Berg.- u. Hüttenw.*, 1910, 58, 549), a secondary action occurring whereby the ammonium salts become oxidised with evolution of nitrogen.

During the attack of gold-silver alloys by aqua regia in the presence of ammonium chloride and nitrate, it often happened

that purplish-brown crystals separated in the liquid. When water was added, they disappeared, and nothing remained but silver chloride. A specially good yield of these crystals was obtained when 2 grams of an alloy of the composition Au 625, Ag 375 were treated with a mixture consisting of 10 grams of ammonium chloride, 3 grams of ammonium nitrate, 5 c.c. of concentrated nitric acid, and 15 c.c. of concentrated hydrochloric acid. The alloy, in the form of thin sheet, was heated gently in a beaker with the above mixture. When all the metal was dissolved, the bottom of the beaker was found to be covered with very small, purplish-brown crystals. They were instantly decomposed by water, with the formation of silver chloride and chloroauric acid, but were found to be fairly stable in concentrated hydrochloric acid.

When prepared in this way, it was found difficult to prevent the crystals being contaminated with ammonium chloride. The following method was therefore devised.

*Preparation of the Salt.*—Twenty-five grams of gold were dissolved in 50 c.c. of nitric acid and 150 c.c. of hydrochloric acid, the liquid being then saturated with about 30–35 grams of ammonium chloride. Three grams of silver nitrate dissolved in 10 c.c. of water were then added, and a copious precipitate of silver chloride formed in the liquid. On adding a few crystals of ammonium chloride, the silver chloride began at once to change into brown crystals. On heating the liquid, the crystals were converted into silver chloride, and, on cooling, again reappeared. This change could be repeated any number of times.

The crystals were allowed to remain in contact with the mother liquor for two or three days to ensure all the silver chloride being converted into the brown salt. The mother liquor was then poured off, saturated with ammonium chloride, and a further amount of silver nitrate added to the solution. A second crop of crystals resulted, and these were heated and allowed to cool as before. The formation of the salt in a hot solution gives rise to larger and better formed crystals than when the preparation is made in a cold solution.

The process was then again repeated, four preparations in all being obtained before the gold became exhausted in the mother liquor. The crystals were freed from the mother liquor in a centrifuge, and afterwards dried at 100°. They were then placed in a Soxhlet thimble and extracted with ether (distilled from sodium) until no more gold was removed. They were afterwards heated at 155° in an air-oven for some time, and the remaining



# 102 THE ACTION OF AQUA REGIA ON GOLD-SILVER ALLOYS, ETC.

traces of ammonium chloride sublimed away. A second treatment with ether followed, after which the crystals were dried and analysed.

Found: Ag=15.58; Au=37.99; NH<sub>4</sub>=6.88; Cl=39.44.

3AgCl, 4AuCl<sub>3</sub>, 8NH<sub>4</sub>Cl requires Ag=15.62; Au=38.06;

NH<sub>4</sub>=6.97; Cl=39.35 per cent.

## Crystallographic Examination.

The crystallographic examination was made by Miss I. E. Knaggs in the Mineralogical Laboratory of the University of Cambridge under the direction of Dr. A. Hutchinson, for whose help and assistance the author wishes to express his gratitude.

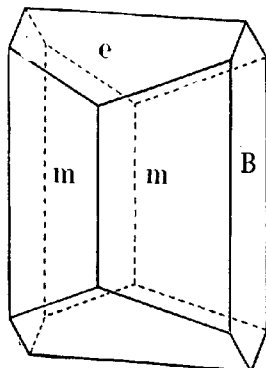
*Crystal System.*—Orthorhombic.

*Class.*—Holohedral.

*Axial Ratio.*— $a:b:c=0.5376:1:0.3210$ .

*Forms Observed.*— $B(010)$ ,  $m(110)$ ,  $e(101)$ .

Angle.	No. of measure- ments.	Limits.	Mean observed.	Calcu- lated.
$mB = (010):(110)$ .....	4	61°43'—61°45'	61°44'	61°44'
$mm'' = (110):(110)$ .....	7	56°28'—56°35'	56°32'	—
$me = (110):(101)$ .....	5	63°10'—63°11'	63°10½'	—
$ee' = (101):(101)$ .....	3	61°39'—61°45'	61°42'	61°41'



*Habit.*—The crystals available for measurement consisted of minute prisms sometimes modified by the brachypinakoid (010), and terminated at either end by the macrodome (101). Some of the preparations consisted of larger crystals showing (110) and

(010) in approximately equal development. These had rough ends and were not suited for accurate measurement.

*Cleavage*.—None observed.

*Optical Characters*.—The crystals were very dark red by reflected light, and owing to their intense absorption it was difficult to make determinations of their optical characters. Some of the smallest and thinnest prisms when mounted so that light traversed them along the *Y* axis were found to be strongly pleochroic, absorption being almost complete for rays vibrating parallel to the axis of *Z*, whilst red light was transmitted fairly freely by vibrations parallel to the axis of *X*. When the crystal was rotated so that light traversed it along the *X* axis, strong absorption was observed of the ray vibrating parallel to *Y* as well as of that vibrating parallel to *Z*. No characteristic interference figure could be observed in convergent light, nor was it possible to determine the refractive indices either by the prism methods or by total reflection. By the immersion method they were found to be high—greater than 1.74.

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## XV.—Intramolecular Rearrangement of the Alkyl-arylamines: Formation of 4-Amino-*n*-butylbenzene.

By JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM.

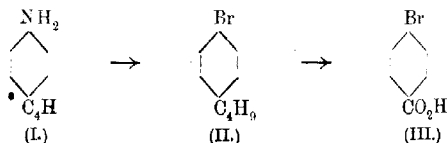
AN important reaction of many of the *N*-substitution products of the arylamines is their rearrangement to *C*-substitution compounds. This change occurs with the majority of the common substituent groups, such as halogen, nitro-, nitroso-, sulphonyl, and alkyl. The intramolecular change of the chloroarylamines may be explained in terms of the variable valency of the nitrogen atom (compare Blanksma, *Rec. trav. chim.*, 1903, **22**, 290; Orton and Jones, *Rep. Brit. Assoc.*, 1910). The formation of *p*-chloroacetanilide from *N*-chloroacetanilide is accompanied by the formation of an additive compound (compare Armstrong, T., 1900, **77**, 1051). The presence of a catalyst is necessary in many molecular changes involving the migration of a nitroso- or nitro-group, as in the production of *p*-nitrosoalkylanilines from nitrosoamines and of nitroanilines from nitroamines. Whilst the bromo- and chloro-aniline derivatives have been thoroughly investigated, as well as the nitroso- and sulphonyl

substituted alkylanilines, the intramolecular change of the alkylarylamines has not been dealt with in such detail.

The earlier work in the production of aminoalkylbenzenes showed that they could be formed either by heating (a) aniline hydrochloride and the alcohol, or (b) the alkylaniline hydrochloride, at temperatures above 300° (compare Hofmann, *Ber.*, 1872, 5, 729). Since methylaniline hydrochloride on heating in a current of hydrogen chloride yields methyl chloride, it has been generally assumed that a somewhat similar reaction would occur in an autoclave or sealed tube on heating the alkylaniline hydrochloride.

On heating *n*-butylaniline hydrochloride in a sealed tube, amino-*n*-butylbenzene was the main product. In addition, ammonia, aniline, and 4-butylamino-*n*-butylbenzene were formed, together with smaller amounts of more highly butylated products. There was also obtained a portion soluble in concentrated hydrochloric acid, and precipitated on dilution, which probably contained diphenylamine derivatives. In addition to the hydrochloride, the alkylaniline zincchloride and certain other compounds with metallic salts also undergo this transformation on heating. The chief product resulting from the intramolecular rearrangement of *n*-butylaniline is, however, 4-amino-*n*-butylbenzene. To explain the formation of this compound from *n*-butylaniline it might be supposed that the latter decomposes partly to aniline and *n*-butyl chloride or butylene; either of the last two might then be supposed to react with aniline. The production of *n*-butyl chloride is probably excluded in the case where zinc chloride replaces the hydrochloric acid. By heating *n*-butylaniline hydrochloride in a sealed tube or in an open flask, a small amount of a gas is obtained, which resembles butylene in being unsaturated. It appears possible that butylene may result as an intermediate product in the change. By heating *n*-butylaniline hydrochloride under atmospheric pressure a certain amount of 4-aminobutylbenzene is produced. If butylene is formed as an intermediate product, some *sec*-butylbenzene should be obtained. An examination of the end-products shows that amino-*sec*-butylbenzene is present, generally, at the most, only in traces.

The orientation of aminobutylbenzene (I), obtained by the intramolecular rearrangement of *n*-butylaniline, was determined by con-

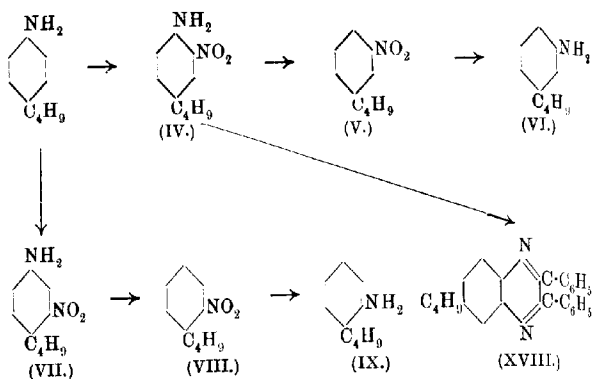


verting the purified amino-derivative into bromobutylbenzene (II), which, on oxidation with chromic acid, gave *p*-bromobenzoic acid (III).

It cannot be assumed with certainty that *n*-butyl alcohol and aniline zincchloride will yield a compound containing a *n*-butyl group. An examination of the literature shows that a rearrangement of the alkyl group often occurs when it is introduced into the benzene ring. The rearrangement of the *n*-butyl chloride and *isobutyl* chloride in the formation of butylbenzenes by the Friedel and Crafts reaction is well established. The rearrangement of alkyl groups in the formation of aminoalkylbenzenes also appears to take place. Effront (*Ber.*, 1884, 17, 2324), by the action of *isobutyl* alcohol on *o*-toluidine hydrochloride, obtained 5-*tert*-butyl-*o*-toluidine, which by the diazo-reaction yielded a phenol identical with that obtained by heating *tert*-butyl chloride, *o*-cresol, and zinc chloride (compare Baur, *Ber.*, 1894, 27, 1615). It is also probable that by the action of *isobutyl* alcohol on aniline hydrochloride amino-*tert*-butylbenzene is obtained. The recorded physical constants of the derivatives of 4-amino-*isobutyl*benzene and 4-amino-*tert*-butylbenzene are practically identical, and doubt must be thrown on their existence as two compounds (compare Studer, *Annalen*, 1882, 211, 234; Senkowski, *Ber.*, 1890, 23, 2412; Malherbe, *Ber.*, 1919, 52, [B], 319).

It became necessary, therefore, to determine the configuration of the butyl group of the primary amine from *n*-butyl alcohol and aniline. By heating aniline zincchloride with *sec*-butyl alcohol an amine was obtained, boiling at 240°, or 20° lower than that obtained from the normal alcohol, and yielding a different series of derivatives. As there was only a small quantity of this amine available it was not possible to determine the orientation of the butyl groups. Any doubt that the primary amine from *n*-butyl alcohol boiling at 258° was not a normal derivative was removed by preparing from it the other two monoamino-compounds. A comparison of the derivatives of the amines thus prepared shows that the amine from *sec*-butyl alcohol differs from the one from *n*-butyl alcohol in the configuration of the butyl group.

By the nitration of 4-acetyl-amino-*n*-butylbenzene, followed by hydrolysis, 3-nitro-4-amino-*n*-butylbenzene (IV) was obtained as a red solid of low melting point. The orientation of the nitro-group was determined by converting the compound into a diamine, which condensed with benzil to yield 2:3-diphenyl-6-*n*-butylquinoraline (XVII). On eliminating the amino-group from 3-nitro-4-amino-*n*-butylbenzene, 3-nitro-*n*-butylbenzene (V) was obtained as a pale yellow oil boiling at 275—277°.

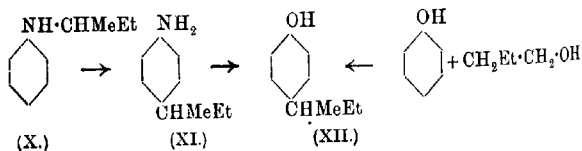


Nitration of 4-amino-*n*-butylbenzene in the presence of sulphuric acid gave 2-nitro-4-amino-*n*-butylbenzene (VII), melting at 52°, which by the diazo-reaction yielded 2-nitro-*n*-butylbenzene (VIII), a yellow oil distilling with some decomposition. Reduction of 2-nitro- and 3-nitro-*n*-butylbenzenes gave primary amines, the derivatives of which are distinct from those obtained from the primary amine boiling at 240° from *sec*-butyl alcohol. It must be concluded, therefore, that in the intramolecular transformation of *n*-butyl-aniline 4-amino-*n*-butylbenzene is obtained.

The following table shows clearly the difference between the amines obtained :

	Acetyl compound,	Benzoyl compound,
	m. p.	m. p.
2-Amino- <i>n</i> -butylbenzene .....	100°	—
3-Amino- <i>n</i> -butylbenzene .....	Not obtained	68°
	crystalline.	
4-Amino- <i>n</i> -butylbenzene .....	105°	126°
4-Amino- <i>sec</i> -.butylbenzene ...	126°	—

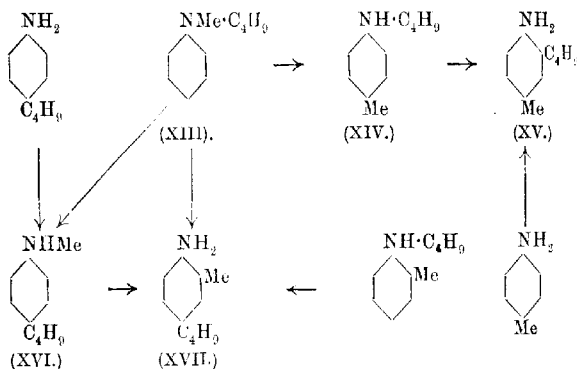
Although *n*-butyl alcohol reacts with aniline zincchloride to yield 4-amino-*n*-butylbenzene, it gives with phenol, in the presence of zinc chloride, hydroxy-*sec*-.butylbenzene. The constitution of the latter compound was shown by its identity with the hydroxy-derivative obtained from 4-amino-*sec*-.butylbenzene (XI) by the aid of the diazo-reaction.



It has been shown by Mailhe and Godon (*Compt. rend.*, 1918, 166, 467) that methylaniline and methyltoluidine are stable at moderately high temperatures, as they may be produced by passing a mixture of methyl alcohol and the primary arylamine over a suitable catalyst heated to 400°. No intramolecular rearrangement is observed when methyl- or ethyl-aniline is passed over heated nickel; instead, a decomposition into aniline and methane or ethylene occurs (Sabatier and Gaudion, *Compt. rend.*, 1917, 165, 309). It has been found that *n*-butylaniline may be heated for several hours at 240–260° without the production of any amino-butylbenzene. Furthermore, the addition of substances which show no tendency to combine with butylaniline, such as calcium sulphate, sodium chloride, or silica, does not bring about any migration of the alkyl group to the nucleus. The formation of 4-amino-*n*-butylbenzene from *n*-butylaniline has been observed to take place only when a substance is added which combines with butylaniline. Substances such as hydrochloric acid, zinc chloride, cobalt chloride, and cadmium chloride have been chiefly employed, and with all these salts the additive compounds have been isolated. It appears that for intramolecular rearrangement of the alkylarylamines to occur, the presence of a substance which is capable of uniting with the amino-group is necessary.

The rearrangement of *n*-butylaniline cannot be satisfactorily explained by assuming the intermediate formation of either butyl chloride or butylene. Orton (*loc. cit.*) has suggested that aminobenzenes and their *N*-substituted derivatives are capable of existing as dynamic isomerides. It is possible that the transference of the alkyl group to the nucleus might occur during one of these phases. To attempt to explain the intramolecular rearrangement of alkylarylamines, the alkyl groups attached to the aminic nitrogen are assumed tentatively to exist in a state of oscillation, following a system of vibration which is definite as long as the external conditions remain constant. The calling into play of the residual valency of the nitrogen atom will have the effect of introducing more groups round the nitrogen atom, with the result that a rearrangement of the alkyl groups may occur. The disturbing effect will depend on several factors, such as the space occupied by each group, its vibration path, and also the polarity of the group. The groups already attached to the nitrogen will have the effect of hindering the entry of another group, corresponding with the space occupied by them. They will also tend to be displaced farther away from the nitrogen atom according to the hindrance produced by them, and there will be a tendency for the alkyl groups to be removed in the order of their steric relations to one another.

Experiments were carried out in order to measure the relative ease with which differing alkyl groups were expelled from the alkyl anilines. The earlier measurements were made by heating the monomethyl- and monobutyl-anilines separately in sealed tubes under similar conditions, so far as possible, with various substances. The results indicate that *n*-butylaniline undergoes intramolecular change the more readily, but the method is open to several objections. It was impossible to ensure absolutely identical conditions for each substance, such as the same temperature and pressure inside each tube. It is also likely that in the formation of the additive compounds of the alkylanilines, steric effects may have an influence, so that the rearrangement caused in the molecule may be counterbalanced to some extent by the steric hindrance due to the alkyl group. To overcome these probable sources of error the intramolecular rearrangement of dissimilarly substituted tertiary alkylanilines has been investigated. Methyl-*n*-butylaniline (XIII) was heated in a sealed tube in the presence of hydrogen chloride, zinc chloride, or cobalt chloride. The products of the rearrangement should then indicate whether the larger alkyl groups are the more readily removed. Thus methyl-*n*-butylaniline should yield as a first step methylaminobutylbenzene (XVI) or butyltoluidine (XIV), according to whether the butyl or the methyl group is the more mobile.



The constitution of the product was determined by dissolving the mixture of amines in dilute hydrochloric acid and adding in slight excess a solution of sodium nitrite. The secondary amines were removed as nitrosoamines, which could be converted into solid nitro-derivatives. Any diazonium salt in the solution was converted into the corresponding azo- $\beta$ -naphthol derivative, which

would serve to identify the primary amine originally present. An examination of the products of nitration of the secondary amines resulting from the intramolecular rearrangement of methyl-*n*-butylaniline indicated that a mixture was present, from which 3:5-dinitro-*n*-butyl-*p*-toluidine and 2:4:6-trinitrophenylmethylnitroamine were isolated in small quantities. It has not yet been possible to determine the complete composition of the mixture.

The *azo-β-naphthol* compounds were reduced, yielding the original primary amines present after intramolecular change had taken place. Analytical results showed that these amines were aminomethylbutylbenzenes, although in one case *p*-tolueneazo-*β*-naphthol was isolated in small amount by recrystallisation of the *azo-β-naphthols*. It appears, therefore, that in the reaction both the methyl and butyl groups have undergone intramolecular rearrangement, and until a method has been elaborated for determining the composition of the products it is not possible to determine accurately the relative ease with which the different alkyl groups are removed.

The elimination of alkyl groups of alkylanilines on heating in a current of hydrogen chloride was also investigated. The secondary amines present in the mixture were isolated as nitrosoamines, and these were nitrated in glacial acetic acid by means of fuming nitric acid and converted into the corresponding trinitrophenylalkylnitroamines. It was found that methyl-*n*-butylaniline yielded a mixture of secondary amines, and 2:4:6-trinitrophenylmethylnitroamine was isolated from the mixture of nitroamines. The melting point of the nitration product was lower than either that of trinitrophenylmethylnitroamine or the corresponding butyl derivative, and was probably a mixture containing these two compounds.

In experiments on the elimination of alkyl groups from dissimilarly substituted alkylarylamines it is essential to use a pure tertiary amine, unmixed with any secondary amine. The methyl-*n*-butylaniline employed was purified by fractionation, followed by heating it with phenylcarbimide. The boiling point of the amine obtained in this way differed considerably from that recorded by Komatsu (*Mem. Coll. Sci. and Eng. Kyoto Imp. Univ.*, 1912, **3**, 371), who also prepared this amine. He records the boiling point as 225–230°, and states that it yields a picrate melting at 143°. Methyl-*n*-butylaniline, purified in the manner indicated above, boils at 242.5° and yields a picrate melting at 90°. The melting point of the picrate is thus brought into agreement with those of other tertiary butylanilines.

By increasing the size of the alkyl group in alkylbutylanilines the melting point of the picrate is raised. The following table shows



the effect of displacing the methyl group in methylbutylaniline by larger groups.

Methyl-*n*-butylaniline boils at 242.5°. The picrate melts at 90°.  
 Ethyl-*n*-butylaniline „ 248° „ „ „ 100°.  
 Di-*n*-butylaniline „ 260–263° „ „ „ 125°.

The nitration of tertiary alkyanilines was also studied. On nitrating methylbutylaniline under vigorous conditions, the principal product is 2:4:6-trinitrophenylmethylnitroamine, showing that the larger group has been eliminated. Meldola and Hollely (T., 1915, 107, 610) have found that in the nitration of acetylated *as*-dialkylphenylenediamines a similar action occurs, the larger groups being removed in the nitration, in preference to the smaller groups.

On nitrating ethyl-*n*-butylaniline both trinitrophenylethylnitroamine and trinitrophenyl-*n*-butylnitroamine are produced. The difference in the relative proportions of the two products of the nitration appears to be less than in the case of methyl-*n*-butylaniline.

Trinitrophenylmethylnitroamine is also obtained on nitrating dimethylaniline under vigorous conditions. Toward the end of the operation there is the usual vigorous effervescence due to the elimination of the methyl group as carbon dioxide. In nitrating di-*n*-butylaniline under similar conditions there is practically no effervescence, and from the mixture after nitration a volatile fatty acid was isolated, which was identified as *n*-butyric acid by means of its distillation constant.

#### EXPERIMENTAL.

##### *The Amino-derivative of *n*-Butylbenzene: 4-Amino-*n*-butylbenzene.*

In the preparation of 4-amino-*n*-butylbenzene, *n*-butyl alcohol was allowed to react with aniline in the presence of a suitable condensing agent, such as zinc chloride. Approximately molecular quantities of aniline and dry *n*-butyl alcohol were mixed with fused zinc chloride (0.5 mol.), and the mixture was heated in an electrically wound autoclave for twenty-four hours at 230–240°. The product was washed first with water to remove uncombined zinc chloride and finally with ether or light petroleum (b. p. 80–100°). In this way secondary amines and other by-products were removed, leaving behind the zincchlorides of the primary amines, from which a mixture of these amino-compounds was obtained by treatment with warm concentrated sodium hydroxide solution. Fractionation of the mixture of bases yielded 4-amino *n* butylbenzene. By using

amounts of zinc chloride less than the molecular proportion—even as low as one-seventh of the amount quoted above—4-amino-*n*-butylbenzene was still produced, but the yield was not so good.

The *hydrochloride* is precipitated on adding an excess of concentrated hydrochloric acid to an aqueous suspension of the base. It is readily soluble in water or alcohol, but only sparingly so in an excess of hydrochloric acid:

0.1063 gave 6.9 c.c.  $N_2$  at  $21^\circ$  and 751 mm.  $N=7.5$ .\*

0.1420 „ 0.1093 AgCl.  $Cl=19.0$ .

$C_{10}H_{15}N, HCl$  requires  $N=7.5$ ;  $Cl=19.1$  per cent.

The *hydrobromide* crystallises from aqueous solution containing free hydrobromic acid in large, white plates. It is readily soluble in water or alcohol:

0.0785 gave 0.0654 AgBr.  $Br=34.6$ .

$C_{10}H_{15}N, HBr$  requires  $Br=34.7$  per cent.

The *sulphate* crystallises from moist ether in a felted mass of white crystals. It is sparingly soluble in water:

0.1002 gave 6.1 c.c.  $N_2$  at  $20^\circ$  and 737 mm.  $N=6.9$ .

0.3502 „ 0.2058  $BaSO_4$ .  $H_2SO_4=24.7$ .

$(C_{10}H_{15}N)_2 \cdot H_2SO_4$  requires  $N=7.1$ ;  $H_2SO_4=24.7$  per cent.

From warm alcohol it separated as a mass of colourless crystals which under the microscope had the appearance of interlaced laths.

The *platinichloride* is a pale brownish-yellow powder, sparingly soluble in water, and more readily so in alcohol. It crystallises from absolute methyl alcohol in small needles melting and decomposing at  $200-202^\circ$ :

0.1203 gave 0.0330 Pt.  $Pt=27.4$ .

$(C_{10}H_{15}N)_2 \cdot H_2PtCl_6$  requires  $Pt=27.6$  per cent.

The *acetyl* derivative, obtained from 4-amino-*n*-butylbenzene by the action of acetic anhydride, crystallises from alcohol in white plates melting at  $105^\circ$ :

0.1426 gave 8.8 c.c.  $N_2$  at  $17^\circ$  and 755 mm.  $N=7.3$ .

$C_{12}H_{17}ON$  requires  $N=7.3$  per cent.

The *benzoyl* derivative, obtained by the Schotten-Baumann reaction, crystallises from alcohol in bulky groups of fine needles melting at  $126^\circ$ :

0.1015 gave 4.65 c.c.  $N_2$  at  $17^\circ$  and 748 mm.  $N=5.3$ .

$C_{17}H_{19}ON$  requires  $N=5.5$  per cent.

\* In the nitrogen estimations recorded in this paper, the gas was measured over 40 per cent. potassium-hydroxide solution, and the pressure has been corrected for vapour tension.

*α*-Phenyl-β-4-*n*-butylphenylcarbamide,  $C_4H_9 \cdot C_6H_4 \cdot NH \cdot CO \cdot NHPh$ .

4-Amino-*n*-butylbenzene was treated with a solution of one molecular proportion of phenylcarbimide dissolved in light petroleum (b. p. 60–80°), and after remaining at the ordinary temperature for two or three hours the precipitate was collected, washed several times with small quantities of light petroleum, and dried:

0.1002 gave 0.2790  $CO_2$  and 0.0678  $H_2O$ .  $C=75.9$ ;  $H=7.5$ .

0.1012 „ 9.1 c.c.  $N_2$  at 20° and 757 mm.  $N=10.5$ .

$C_{17}H_{20}ON_2$  requires  $C=76.1$ ;  $H=7.5$ ;  $N=10.4$  per cent.

It crystallises from aqueous alcohol in bulky masses of small, white needles melting at 160°. It is soluble in ether, acetone, ethyl acetate, or glacial acetic acid, but sparingly so in water or light petroleum.

#### 4-Bromo-*n*-butylbenzene.

The orientation of the butyl group was determined by converting the amino-*n*-butylbenzene into a derivative that could yield a substituted benzoic acid by oxidation. For this purpose the amino-group was displaced by bromine by the Sandmeyer reaction. 4-Amino-*n*-butylbenzene was dissolved in three molecular proportions of hydrobromic acid and diazotised by the addition of sodium nitrite solution. On adding a solution of cuprous bromide in hydrobromic acid, followed by distillation in a current of steam, 4-bromo-*n*-butylbenzene was obtained as a pale yellow oil of pleasant, ethereal odour, denser than water, and boiling at 242–243°/755 mm.:

0.0853 gave 0.1762  $CO_2$  and 0.0460  $H_2O$ .  $C=56.4$ ;  $H=6.0$ .

$C_{10}H_{13}Br$  requires  $C=56.3$ ;  $H=6.1$  per cent.

That the bromo- and alkyl groups are in the para-position follows from the production of *p*-bromobenzoic acid by oxidation. Half a gram was heated in a sealed tube with 12 c.c. of a 6 per cent. solution of chromic acid for seven hours at 150–200°. There was practically no pressure on opening the tube, which contained a green, amorphous mass together with tarry matter and some white, glistening, needle-shaped crystals. The contents of the tube were rendered alkaline, and after removing the suspended matter, a grey solid was precipitated on adding dilute sulphuric acid. It was purified by dissolving in sodium carbonate solution, and any traces of volatile bromo-compounds were removed by means of a current of steam. The addition of dilute hydrochloric acid precipitated a white solid which crystallised from ether in small needles melting at 250°. This melting point is almost identical with that recorded for *p*-bromobenzoic acid (251°), and is considerably higher than those of the other two monobromobenzoic acids.

*Diazoamino-4-n-butylbenzene.*

The base (1 mol.) was dissolved in glacial acetic acid (3 mols.) and the solution diluted. On adding sodium nitrite solution, a yellow, semi-solid mass separated which quickly became hard. The *diazoamino-4-n-butylbenzene* was collected and, after washing several times with water to remove any traces of nitrous acid, crystallised from light petroleum, from which it separated in masses of slender, sulphur-yellow needles melting at  $75^{\circ}$ :

0.0743 gave 9.0 c.c.  $N_2$  at  $24^{\circ}$  and 742.5 mm.  $N=13.7$ .

$C_{20}H_{27}N_3$  requires  $N=13.6$  per cent.

When exposed to the light it darkened slowly.

*4-n-Butylbenzeneazo- $\beta$ -naphthol.*

A solution of the hydrochloride of the base was diazotised and, after removing the excess of nitrous acid by means of carbamide, it was poured into an alkaline solution of  $\beta$ -naphthol. The red azo-compound crystallised from hot alcohol in bright red bunches of slender needles melting at  $80^{\circ}$ :

0.1088 gave 9.8 c.c.  $N_2$  at  $15.3^{\circ}$  and 741 mm.  $N=9.4$ .

$C_{20}H_{20}ON_2$  requires  $N=9.2$  per cent.

*4-n-Butylbenzeneazo- $\beta$ -naphthol* is insoluble in a 30 per cent. solution of potassium hydroxide. It dissolves in concentrated sulphuric acid with the production of a brilliant purple colour, which gives place to a faint brown coloration on dilution.

*4-n-Butylbenzeneazophenyl- $\beta$ -naphthylamine.*

This derivative was prepared by adding a diazotised solution of 4-amino-*n*-butylbenzene, freed from excess of nitrous acid, to one molecular proportion of phenyl- $\beta$ -naphthylamine dissolved in acetic acid. An excess of sodium acetate was then added, and the red product was allowed to remain at the ordinary temperature for two to three hours, with occasional stirring. Water was added to complete the precipitation of the azo-compound, which was collected and purified after being washed with warm water:

0.1080 gave 10.2 c.c.  $N_2$  at  $17^{\circ}$  and 750 mm.  $N=11.1$ .

$C_{26}H_{25}N_3$  requires  $N=11.1$  per cent.

It is readily soluble in chloroform, benzene, or ether. In the presence of a small amount of ether the azo-compound dissolves in concentrated hydrochloric acid to yield an intense purplish-blue solution. After some time the colour disappears with the production of a dark precipitate which becomes red after keeping for a

further period. Concentrated sulphuric acid dissolves it with the production of an intense dark blue coloration, becoming red on dilution.

*4-n-Butylbenzeneazobenzoylacetone.*

A diazotised solution of 4-amino-*n*-butylbenzene (1 mol.), freed from nitrous acid by means of carbamide, was added to an alcoholic solution of benzoylacetone (1 mol.). The addition of sodium acetate produced a bright yellow turbidity, from which a dark-coloured oil separated. On keeping overnight in the ice-chest the oil solidified to a mass of dark yellow crystals which were collected, dried on a porous plate, and recrystallised. The compound separated from ether in stellate groups of yellow crystals melting at 97—100°:

0.1588 gave 12.2 c.c.  $N_2$  at 18° and 747 mm.  $N=8.9$ .

$C_{20}H_{22}O_2N_2$  requires  $N=8.7$  per cent.

The substance is soluble in alcohol or ether, and dissolves in sulphuric acid with the production of a brown colour, giving place to a yellow opalescence on dilution. Sulphuric acid containing a small amount of dissolved chromic acid also produces a similar coloration.

*4-n-Butylbenzeneazo-2:7-dihydroxynaphthalene.*

This compound was obtained as a dark red powder on adding a solution of the diazotised amine to an alcoholic solution of 2:7-dihydroxynaphthalene in the presence of an excess of sodium acetate. It was purified by washing with a dilute aqueous solution of sodium hydroxide, followed by extraction with chloroform. It crystallised from hot glacial acetic acid in small, bronze-coloured crystals melting at 200—201°:

0.1588 gave 12.2 c.c.  $N_2$  at 18° and 747 mm.  $N=8.9$ .

$C_{20}H_{20}O_2N_2$  requires  $N=8.7$  per cent.

*4-Hydroxy-*n*-butylbenzene.*

4-Amino-*n*-butylbenzene (9 grams) was added to an aqueous solution containing sulphuric acid in excess (five molecular proportions), and, after cooling, diazotised by the addition of sodium nitrite. The mixture was stirred continuously, when the suspended sulphate gradually passed into solution. The solution was filtered to remove any unchanged sulphate, treated with a large excess of concentrated sulphuric acid, and subsequently distilled in a current of steam. 4-Hydroxy-*n*-butylbenzene passed over as a pale yellow oil, and was

obtained pure by distillation. It is an almost colourless oil, possessing a faint phenolic odour, and boiling at  $248^{\circ}/765$  mm.:

0.0818 gave 0.2387  $\text{CO}_2$  and 0.0686  $\text{H}_2\text{O}$ .  $\text{C}=79.6$ ;  $\text{H}=9.3$ .

$\text{C}_{10}\text{H}_{14}\text{O}$  requires  $\text{C}=79.95$ ;  $\text{H}=9.4$  per cent.

*4-n-Butylphenyl Phenylcarbamate*,  $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$ .

4-Hydroxy-*n*-butylbenzene was heated on the water-bath with slightly more than one molecular proportion of phenylcarbimide. On cooling, the solid mass was passed on a porous tile and crystallised from alcohol, from which it separated in white needles melting at  $115^{\circ}$ :

0.1059 gave 4.7 c.c.  $\text{N}_2$  at  $20^{\circ}$  and 744 mm.  $\text{N}=5.0$ .

$\text{C}_{17}\text{H}_{19}\text{O}_2\text{N}$  requires  $\text{N}=5.2$  per cent.

*2-Nitro-4-amino-n-butylbenzene*.\*

4-Amino-*n*-butylbenzene was dissolved in two hundred times its weight of concentrated sulphuric acid and, after cooling to  $-5^{\circ}$ , the calculated amount of nitric acid (1 mol.), dissolved in three times its weight of sulphuric acid, was added gradually. During the addition of the acid the mixture was continually stirred, and the temperature not allowed to rise above  $5^{\circ}$ . After eighteen hours the mixture was poured into ice-water, when a sparingly soluble sulphate was precipitated, which was collected and decomposed by the addition of aqueous ammonia. In this way a brown, crystalline solid was obtained consisting of *2-nitro-4-amino-n-butylbenzene*. A further quantity was isolated by treating the acid filtrate with aqueous ammonia and extracting the solution with ether. It was obtained pure by dissolving it in aqueous methyl alcohol, and precipitating with water, followed by recrystallisation from warm light petroleum (b. p.  $80$ — $100^{\circ}$ ). It forms golden-yellow scales, readily soluble in ether and melting at  $52^{\circ}$ :

0.0739 gave 9.3 c.c.  $\text{N}_2$  at  $17.5^{\circ}$  and 735 mm.  $\text{N}=14.5$ .

$\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2$  requires  $\text{N}=14.4$  per cent.

No evidence was obtained of the existence of the other isomeride.

The *hydrochloride* was obtained as a white precipitate by adding hydrochloric acid to an ethereal solution of the base and evaporat-

\* The nitration of *n*-butyl-*p*-toluidine has been previously described as yielding 2-nitro-*n*-butyl-*p*-toluidine as a red oil (T., 1918, 113, 988). On keeping over the winter it solidified to a mass of bright red crystals melting at  $18$ — $19^{\circ}$ . By converting the substance into its hydrochloride, crystallising from alcohol, and decomposing with aqueous ammonia, 2-nitro-*n*-butyl-*p*-toluidine was obtained in large, rectangular, red plates which melted at  $19^{\circ}$ .

ing the ether. It crystallises from warm absolute methyl alcohol in masses of slender, colourless needles. On heating, the colour changes to yellow. A specimen melted at 190—195° after immersion in the bath at 150°, a rapid darkening in colour taking place at 185—190°:

0.1017 gave 0.0638 AgCl. Cl=15.5.

$C_{10}H_{14}O_2N_2.HCl$  requires Cl=15.4 per cent.

The *sulphate* is sparingly soluble in dilute sulphuric acid. It crystallises from warm alcohol containing some sulphuric acid in small, white plates which are hydrolysed by water:

0.0811 gave 6.35 c.c.  $N_2$  at 13.2° and 761 mm. N=9.4.

$C_{12}H_{16}O_3N_2.H_2SO_4$  requires N=9.6 per cent.

#### 2-Nitro-n-butylbenzene.

2-Nitro-4-aminobutylbenzene (2.5 grams) was diazotised in aqueous alcoholic solution in the presence of sulphuric acid, a small amount of insoluble matter was removed, and the diazo-group was eliminated by heating with an excess of alcohol, when 2-nitro-n-butylbenzene was obtained. It is a pale yellow oil possessing a characteristically pleasant odour. It is readily volatile in steam, and apparently so in alcohol vapour, for on removing the alcohol by distillation after eliminating the diazo-group, appreciable amounts of the nitro-compound were obtained in the alcoholic distillate.

It distils with some decomposition at about 260° under the ordinary pressure:

0.0814 gave 5.4 c.c.  $N_2$  at 20° and 746 mm. N=7.6.

$C_{10}H_{13}O_2N$  requires N=7.8 per cent.

#### 2-Amino-n-butylbenzene.

Reduction of the nitro-compound was effected by means of zinc dust or tin foil and hydrochloric acid. The amine was isolated by extraction with ether after rendering the acid liquid alkaline. 2-Amino-n-butylbenzene is a yellow oil, possessing a rather unpleasant odour recalling that of aniline:

0.0746 gave 5.9 c.c.  $N_2$  at 16° and 750 mm. N=9.3.

$C_{10}H_{13}N$  requires N=9.4 per cent.

The *acetyl* derivative crystallises from warm aqueous methyl alcohol in masses of small, white needles melting at 100°:

0.0819 gave 5.5 c.c.  $N_2$  at 20.5° and 749 mm. N=7.7.

$C_{12}H_{17}ON$  requires N=7.3 per cent.

The melting point of this compound is very close to that of

4-acetylamino-*n*-butylbenzene. It was shown to be distinct from that substance, for a mixture of these acetyl derivatives commenced to melt at 75° and had completely melted at 85°.

### 3-Nitro-4-amino-*n*-butylbenzene.

The most convenient method of obtaining this compound in a pure state was to nitrate 4-acetylamino-*n*-butylbenzene by means of fuming nitric acid, afterwards eliminating the acetyl group.

3-Nitro-4-acetylamino-*n*-butylbenzene.—The acetyl compound (2 grams) was dissolved in 20 c.c. of glacial acetic acid, the solution cooled to -5°, and 15 grams of nitric acid (D 1.5) were added slowly, so that the temperature did not rise above 5°. After an hour the mixture was poured into ice-water, and the yellow precipitate collected. The nitro-compound is soluble in most of the common organic solvents except light petroleum, and crystallises very readily from hot alcohol in slender, canary-yellow needles melting at 76°:

0.0649 gave 6.8 c.c. N<sub>2</sub> at 20° and 746.6 mm. N=12.0.

C<sub>12</sub>H<sub>16</sub>O<sub>3</sub>N<sub>2</sub> requires N=11.9 per cent.

Titration with Titanous Chloride.—0.01522 required 16.6 c.c. TiCl<sub>3</sub> (1 c.c.=0.001297 gram Fe). Calc. as C<sub>12</sub>H<sub>16</sub>O<sub>3</sub>N<sub>2</sub>=100.4 per cent.

On triturating it in a mortar with a 50 per cent. solution of potassium hydroxide the colour changed from pale yellow to deep brown. After remaining for some time there was still a considerable amount of the unchanged acetyl derivative together with some 3-nitro-4-amino-*n*-butylbenzene. The latter compound was obtained more conveniently by hydrolysis with alcoholic hydrogen chloride. To the nitroacetyl compound dissolved in ten times its weight of alcohol, an amount of hydrochloric acid, insufficient to precipitate the nitro-compound, was added, and the mixture was heated under reflux until, on pouring into dilute hydrochloric acid, no precipitate was obtained. On evaporation, 3-nitro-4-amino-*n*-butylbenzene was left as a reddish-brown oil, which solidified in the ice-chest to a mass of reddish-yellow needles melting at about 13°. The substance was purified by converting it into the hydrochloride, and decomposing this with water or dilute ammonia:

0.0880 gave 11.0 c.c. N<sub>2</sub> at 18.5° and 745 mm. N=14.4.

C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub> requires N=14.4 per cent.

Titration with Titanous Chloride.—0.01038 required 13.3 c.c. TiCl<sub>3</sub> (1 c.c.=0.001344 gram Fe). Calc. as C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub>=100.8 per cent.

The hydrochloride crystallises from a mixture of alcohol and ether in flat, shining plates. It is readily hydrolysed by water.



Reduction of the base by adding zinc dust to a warm solution in hydrochloric acid gave 4-*n*-butyl-*o*-phenylenediamine as a viscous oil which is very readily oxidised on exposure to the air. On this account it was not isolated in a pure state for analysis, and the condensation product with benzil was prepared from its solution.

3-Nitro-4-amino-*n*-butylbenzene (1.4 grams) was dissolved in an excess of 50 per cent. aqueous acetic acid, and after raising the solution to the boiling point small quantities of zinc dust were added until the reduction was complete. Benzil (1.5 grams), dissolved in warm sodium hydrogen sulphite solution, was added and the mixture boiled for five minutes. A reddish-brown oil was produced, which on cooling settled to the bottom of the flask as a semi-solid mass. It was collected and, after pressing on a porous tile, crystallised from hot methyl alcohol. Pale yellow, flocculent masses of small crystals were obtained on rapid cooling and small, pale yellow needles, melting at  $82^{\circ}$ , by slow cooling. By spontaneous evaporation of an ethereal solution, large, well-defined groups of needle-shaped crystals separated:

0.0988 gave 6.8 c.c.  $N_2$  at  $15.0^{\circ}$  and 768 mm.  $N=8.3$ .

$C_{24}H_{22}N_2$  requires  $N=8.3$  per cent.

2:3-Diphenyl-6-*n*-butylquinoraline (XVIII) is readily soluble in chloroform. It dissolves in cold, concentrated sulphuric acid with the production of an orange colour, which on dilution gives place to a white turbidity. It is also soluble in a large excess of concentrated hydrochloric acid, giving a yellow solution.

### 3-Nitro-*n*-butylbenzene.

3-Nitro-4-amino-*n*-butylbenzene was dissolved in hydrochloric acid (2.5 mols.) mixed with an equal volume of alcohol, and the solution cooled to  $-5^{\circ}$ . A slight excess of sodium nitrite solution was added, and after about an hour some red, resinous matter was filtered off and the filtrate heated with an excess of ethyl alcohol under reflux for two hours. The alcohol was evaporated on the water-bath, and the volatile nitro-compound removed from the residue by distillation in a current of steam. 3-Nitro-*n*-butylbenzene was obtained as a yellow liquid having a pleasant odour:

0.0766 gave 5.4 c.c.  $N_2$  at  $20^{\circ}$  and 747 mm.  $N=8.1$ .

$C_{10}H_{13}O_2N$  requires  $N=7.8$  per cent.

The compound distils at  $275^{\circ}/752$  mm. with no appreciable decomposition. It is apparently volatile to some extent in alcohol vapour, for on removing the excess of alcohol from the product of the diazo-reaction some of it was obtained in the distillate. It is

miscible with chloroform, nitrobenzene, pyridine, or light petroleum.

*3-Amino-n-butylbenzene.*

To the nitro-compound suspended in concentrated hydrochloric acid, small pieces of tin foil were added from time to time until the reduction was complete. The tin in solution was removed as sulphide, and after rendering the liquid alkaline with sodium hydroxide solution, the amine was removed by extraction with ether. It was further purified by distillation in a current of steam.

*3-Amino-n-butylbenzene* is a pale yellow oil, lighter than water, and possesses a faint, agreeable odour:

0.1454 gave 12.5 c.c.  $N_2$  at  $25^\circ$  and 727 mm.  $N=9.6$ .

$C_{10}H_{15}N$  requires  $N=9.4$  per cent.

The addition of an excess of warm concentrated hydrochloric acid yielded the *hydrochloride* as an oil which solidified on cooling to an interlaced mass of small, flattened, jagged needles.

The *acetyl* compound was obtained as an oil, which slowly hardened to a vitreous mass on keeping it in a desiccator:

0.0744 gave 4.9 c.c.  $N_2$  at  $25^\circ$  and 745 mm.  $N=7.4$ .

$C_{12}H_{17}ON$  requires  $N=7.3$  per cent.

The *benzoyl* derivative, prepared by the Schotten-Baumann reaction, separates from alcohol in small, white, needle-shaped crystals, which melt at  $68^\circ$ :

0.1610 gave 7.8 c.c.  $N_2$  at  $17^\circ$  and 748 mm.  $N=5.7$ .

$C_{17}H_{19}ON$  requires  $N=5.5$  per cent.

*4-Amino-sec.-butylbenzene.*

To show that no intramolecular rearrangement of the butyl group had occurred when *n*-butyl alcohol and aniline zincchloride interacted, the corresponding amine was prepared from *sec*-butyl alcohol, which was obtained from *n*-butyl alcohol through the intermediate formation of butylene. In the presence of sulphuric acid, butylene yielded *sec*-butyl alcohol, which was obtained pure by repeated fractionation. It boiled at  $99.6-99.9^\circ$ .

Aniline zincchloride was heated with one molecular proportion of *sec*-butyl alcohol in an autoclave at  $180^\circ$  for sixty hours, the product being treated in exactly the same way as described above when *n*-butyl alcohol was used. The mixture of primary amines from the zincchloride was fractionated, and yielded, among other distillates, a fraction boiling between  $230^\circ$  and  $250^\circ$ . On redistilling this portion several times a primary amine was obtained boiling at  $238^\circ/762$  mm. From the mixture of secondary amines soluble

in light petroleum, a primary amine was isolated by means of its sulphate, boiling at  $238^{\circ}$  and identical with the amine obtained from the mixture of primary bases:

0.1909 gave 16.0 c.c.  $N_2$  at  $19.5^{\circ}$  and 740 mm.  $N=9.6$ .

$C_{10}H_{13}N$  requires  $N=9.4$  per cent.

4-Amino-*sec*-butylbenzene, on keeping, slowly changes in colour from very pale yellow to dark red. The diazonium salt gives a red *azo*-compound with  $\beta$ -naphthol in alkaline solution. With bleaching powder solution the amine gave no coloration. The addition of a solution of chromic acid in concentrated sulphuric acid produced a dirty green coloration, changing through purple to wine-red on dilution. Nitric acid added in small amount to the sulphate of the amine suspended in concentrated sulphuric acid coloured the solid matter purple, and the solution yellowish-brown.

The hydrochloride is precipitated from aqueous solution on the addition of an excess of hydrochloric acid:

0.0987 gave 0.0750 AgCl.  $Cl=18.8$ .

$C_{10}H_{15}N \cdot HCl$  requires  $Cl=19.1$  per cent.

The sulphate is sparingly soluble in cold water, but more readily so in hot water, from which it separates in masses of white crystals.

The acetyl derivative crystallises from aqueous alcohol in lustrous, white plates melting at  $125-126^{\circ}$ :

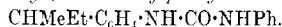
0.1540 gave 10.0 c.c.  $N_2$  at  $19^{\circ}$  and 744 mm.  $N=7.5$ .

$C_{12}H_{17}ON$  requires  $N=7.3$  per cent.

It is soluble in acetone, ether, or ethyl acetate, and sparingly so in water. No coloration is obtained by the addition of a solution of chromic acid in concentrated sulphuric acid.

With fuming nitric acid in glacial acetic acid solution it yields a yellow, crystalline *nitro*-derivative.

*$\alpha$ -Phenyl- $\beta$ -4-*sec*-butylphenylcarbamide,*



This derivative is prepared by the addition of phenylcarbimide to 4-amino-*sec*-butylbenzene. It crystallises from aqueous alcohol in silky needles melting at  $144^{\circ}$ :

0.0730 gave 6.5 c.c.  $N_2$  at  $14^{\circ}$  and 756 mm.  $N=10.6$ .

$C_{17}H_{20}ON_2$  requires  $N=10.4$  per cent.

It is soluble in ether, acetone, or toluene, but only sparingly so in light petroleum (b. p.  $60-80^{\circ}$ ).

In addition to amino-*sec*-butylbenzene, other amines were obtained from the product of the action of heat on the mixture of *sec*-butyl alcohol and aniline zincchloride. At  $270-280^{\circ}$  a fraction

was obtained consisting mainly of a primary amine, which on further purification boiled mainly between  $274^{\circ}$  and  $278^{\circ}$ . This consisted apparently of aminodi-*sec*-butylbenzene. A small quantity of a residue of a still higher boiling point was obtained, but it was not further investigated. The fractions of lower boiling points contained a considerable amount of a secondary amine, which was freed from the greater part of the primary amine by treatment with dilute sulphuric acid. In this manner a fraction was obtained boiling at  $225$ – $235^{\circ}$  consisting chiefly of *sec*-butylaniline, which was obtained in a pure state by the action of *sec*-butyl chloride on aniline. Aniline (1 mol.) was heated under a reflux condenser with *sec*-butyl chloride (1.5 mols.); this contained a small amount of dissolved iodine, and was added gradually over a period extending over twenty-four hours. The purplish-blue product was rendered alkaline, and from the ethereal extract the *sec*-butylaniline was precipitated as the zincchloride, the base being purified by distillation. It distilled at  $224$ – $225^{\circ}/765$  mm. as an almost colourless oil which had a pleasant, floral odour distinct from that of the corresponding *n*-butyl derivative:

0.0928 gave 0.2732  $\text{CO}_2$  and 0.0866  $\text{H}_2\text{O}$ .  $\text{C}=80.3$ ;  $\text{H}=10.4$ .

0.0835 „ 6.7 c.c.  $\text{N}_2$  at  $14^{\circ}$  and 756 mm.  $\text{N}=9.5$ .

$\text{C}_{10}\text{H}_{15}\text{N}$  requires  $\text{C}=80.5$ ;  $\text{H}=10.1$ ;  $\text{N}=9.4$  per cent.

It is miscible with most of the common organic solvents. The addition of a solution of chromic acid in concentrated sulphuric acid led to the production of no characteristic coloration. On adding a small quantity of nitric acid to a solution of the amine in concentrated sulphuric acid a reddish-brown coloration was observed.

The *hydrochloride* was obtained as a hard, crystalline mass by saturating a benzene solution of *sec*-butylaniline with dry hydrogen chloride:

0.1324 gave 0.1030  $\text{AgCl}$ .  $\text{Cl}=19.2$ .

$\text{C}_{10}\text{H}_{15}\text{N}.\text{HCl}$  requires  $\text{Cl}=19.1$  per cent.

It crystallises from warm benzene in hard nodules, which in bulk are grey. It is very readily soluble in water.

By the action of nitrous acid on the solution of the hydrochloride *phenyl-sec-butylnitrosoamine* was obtained as a pale yellow oil, possessing an agreeable odour. It is volatile in steam:

0.0924 gave 12.6 c.c.  $\text{N}_2$  at  $18.7^{\circ}$  and 753 mm.  $\text{N}=15.9$ .

$\text{C}_{10}\text{H}_{14}\text{ON}_2$  requires  $\text{N}=15.7$  per cent.

#### *p*-*sec*-Butylphenol.

On diazotising amino-*sec*-butylaniline sulphate and boiling the solution, nitrogen was evolved, and the liquid assumed a reddish-

brown colour due to the production of *p*-*sec*.-butylphenol. It was purified by distillation in a current of steam, followed by fractionation.

At 238° *p*-*sec*.-butylphenol passed over as a pale oil, solidifying to a mass of long, hair-like, white needles, melting at 59°. The melting point was not altered after two crystallisations from light petroleum. (Estreicher, *Ber.*, 1900, **33**, 436, gives m. p. 53–54°, b. p. 239.5–240.5°/750.6 mm.) The substance is very readily soluble in alcohol or ether, and, when treated with a dilute solution of chromic acid in concentrated sulphuric acid, gives no characteristic coloration, other than the production of a transient red tint. Ferric chloride also gives no coloration. (Found: C=79.9; H=9.9.  $C_{10}H_{14}O$  requires C=79.95; H=9.4 per cent.) It is miscible with most of the common organic solvents. This compound was also obtained, probably in an impure state, by the action of *n*-butyl alcohol on phenol. In this reaction a rearrangement of the alkyl group occurs.

The boiling point of the phenol agrees with that of the substance prepared by the diazo-reaction. It was not, however, obtained crystalline, nor were any crystalline derivatives prepared from it. It seems probable that *p*-*sec*.-butylphenol is not the only product of the interaction between *n*-butyl alcohol and phenol in the presence of zinc chloride.

Phenol (100 grams) was heated with fused zinc chloride (240 grams) and *n*-butyl alcohol (80 grams) for twelve hours. On cooling, the mixture had separated into two layers. The addition of water dissolved the lower layer consisting mainly of zinc chloride, whilst the dark-coloured oil was removed. It consisted chiefly of *p*-*sec*.-butylphenol, together with some ethers which were removed by dissolving the phenol in sodium hydroxide solution. On distillation the main fraction was collected between 235° and 245° as a colourless oil of agreeable odour. Further fractionation gave a colourless, viscous oil distilling at 237–240°.

On the addition of a diazotised solution of  $\beta$ -naphthylamine to a solution of the phenol in dilute potassium hydroxide solution, a brown liquid was obtained, from which a reddish-brown *azo*-compound was isolated on rendering acid and extracting with solvents. It was not, however, obtained in a pure state.

The acetyl derivative, prepared by heating 5 grams of *p*-*sec*.-butylphenol with an excess of fused sodium acetate and 10 grams of acetic anhydride for three hours, was obtained as a colourless oil boiling at 244–246°/760 mm. (Estreicher, *loc. cit.*, gives 255.5°/743.9 mm.).

The *benzoyl* derivative, obtained by the Schotten-Baumann method, is an almost colourless, viscous oil:

0.0686 gave 0.2023 CO<sub>2</sub> and 0.0430 H<sub>2</sub>O. C=80.4; H=7.0.

C<sub>12</sub>H<sub>15</sub>O<sub>2</sub> requires C=80.3; H=7.1 per cent.

By nitrating crude *p*-*sec*.-butylphenol with concentrated nitric acid, mixtures of mono- and dinitro-derivatives were obtained. A better yield of the former was obtained by using dilute nitric acid.

*p*-*sec*.-Butylphenol (2.5 grams) was added to nitric acid (6 grams: D 1.5) and water (9 grams), the mixture being cooled in a stream of cold water. After sixteen hours the supernatant layer of acid was poured off and the residual oil distilled in a current of steam.

*Nitro-p*-*sec*.-butylphenol was obtained in this way as a red oil, which was purified by distillation under diminished pressure, when it distilled at 196–200°/80 mm.:

0.1452 gave 9.0 c.c. N<sub>2</sub> at 16° and 741 mm. N=7.2.

C<sub>10</sub>H<sub>13</sub>O<sub>3</sub>N requires N=7.2 per cent.

The addition of aqueous ammonia precipitated the *ammonium* salt, and solutions of sodium and potassium hydroxides precipitated the corresponding alkali salts.

#### *Reaction with Phenylcarbimide.*

By heating *p*-*sec*.-butylphenol, prepared from *n*-butyl alcohol, at 100° with one molecular proportion of phenylcarbimide, a viscous oil was obtained, which was purified by extracting it several times with light petroleum. It was dried first at 80° for a short time, and finally over solid potassium hydroxide under diminished pressure. On cooling to 0° it was obtained as a brittle solid which became viscous at the ordinary temperature.

#### *Intramolecular Rearrangement of n-Butylaniline.*

The experimental details for the production of 4-amino-*n*-butylbenzene have already been described (p. 110), and it has been mentioned that other substances are produced in the reaction. The primary amines which were separated by the use of zinc chloride were distilled. Aniline was obtained in the first fractions, the amount being dependent on the experimental conditions. The principal fraction was 4-amino-*n*-butylbenzene, but there was still a residue of amines boiling at above 270°; this, on distillation, proved to be a complex mixture, from which a primary amine boiling at 295–300° was isolated, and was probably 4-amino-1:3-di-*n*-butylbenzene:

0.0900 gave 5.3 c.c.  $N_2$  at  $20^\circ$  and 737 mm.  $N=6.7$ .

$C_{14}H_{23}N$  requires  $N=6.8$  per cent.

It yields a sparingly soluble *sulphate*, and after treatment with nitrous acid in the cold, combines with alkaline  $\beta$ -naphthol with the formation of an *azo*-compound. A fraction of still higher boiling point which also contains a primary amine was not investigated.

The ethereal washings of the zincichloride (p. 110) obtained by the action of *n*-butyl alcohol on aniline zincichloride were shaken with dilute sodium hydroxide solution to remove a portion (*A*) containing phenolic substances and then several times with dilute hydrochloric acid to remove a portion (*B*) containing secondary and tertiary amines. There was finally obtained an ethereal solution containing for the most part substances which are soluble only in concentrated hydrochloric acid, and are precipitated on dilution. These substances boil at above  $290^\circ$  under the ordinary pressure, and their sulphuric solution in the presence of nitrous acid develops an intense bluish-black colour. The behaviour and properties of these substances suggest that they may be diphenylamine derivatives, but they were not further investigated. The separated portions were examined as follows: (*A*) The phenolic substances were isolated by acidifying the alkaline solution and extracting with ether. They appeared to be a mixture of phenol and butylphenol, for on distillation two definite fractions were obtained, one at about  $200-210^\circ$ , and the principal fraction at  $240-245^\circ$ . These phenols do not appear to be constant constituents of the products of the reaction being usually present at the most in small amounts.

(*B*) The amines on distillation gave a secondary amine boiling at  $235-245^\circ$ , with small amounts of a primary amine at  $255-265^\circ$ , which was shown to be 4-amino-*n*-butylbenzene. Between  $275^\circ$  and  $290^\circ$  a secondary amine, probably 4-*n*-butylamino-*n*-butylbenzene, was collected in an impure condition. It was dissolved in dilute hydrochloric acid and treated with nitrous acid, when 4-*n*-butylphenyl-*n*-butylnitrosoamine separated as a yellowish-red oil, volatile in steam, and having a pleasant odour:

0.0703 gave 7.4 c.c.  $N_2$  at  $17.8^\circ$  and 744 mm.  $N=12.1$ .

$C_{14}H_{22}ON_2$  requires  $N=12.0$  per cent.

The amount of this secondary amine present in the mixture resulting from the action of *n*-butyl alcohol on aniline zincichloride is usually small, and the yield appears to depend on the experimental conditions. The residue of higher boiling point yielded, at about  $300^\circ$ , aminodibutylbenzene, which was isolated as a sparingly soluble sulphate, and a mixture of amines, yielding fractions up to  $360^\circ$ . Amines of still higher boiling points were obtained on dis-

tilling under diminished pressure until only a semi-carbonised mass remained in the flask. This distillate, which contained primary, secondary, and tertiary amines, was not further investigated, but no doubt consisted of amino-compounds containing more than two butyl groups in the nucleus.

The formation of 4-amino-*n*-butylbenzene by the action of dry *n*-butyl alcohol on aniline zincchloride may be due to the initial formation of *n*-butylaniline, followed by intramolecular change, or to the direct entry of the butyl group into the nucleus. The former suggestion agrees better with the experimental results, for by reducing the time of the reaction and the temperature at which it occurs *n*-butylaniline is obtained in greater amount than usual, whilst the yield of 4-amino-*n*-butylbenzene is much smaller. In one experiment the temperature was allowed to rise gradually to 180—200° over a period of six hours. The products were aniline and *n*-butylaniline, only a small quantity of 4-amino-*n*-butylbenzene being formed.

It was also found that pure *n*-butylaniline, in the presence of zinc chloride and also certain other salts, underwent intramolecular change on heating at temperatures between 200° and 240° for about six to eight hours.

#### *n*-Butylaniline and Cobalt Chloride.

*n*-Butylaniline (4·5 grams) was heated in a sealed tube at temperatures between 200° and 240° for seven hours with anhydrous cobalt chloride (2 grams). There was only a slight pressure on opening the tube, and the contents, which were initially pale green, changed to a deep blue, crystalline mass. After treatment with warm water and dilute sodium hydroxide solution the mixture of amines had the following composition:

Primary amine ... ..	62 per cent.
Secondary amine ... ..	14 " "
Bases insoluble in dilute hydrochloric acid ... ..	23 " "

The primary amine gave an acetyl compound melting at 103° after one crystallisation, which was identical with 4-acetylamino-*n*-butylbenzene.

Other experiments were carried out, by heating pure *n*-butylaniline under pressure in the presence of various substances, such as zinc chloride and sodium chloride. The results obtained are given in the following table:



Substance, added.	Duration of heating, 8 hours.	Percentage composition of resulting amines.		
		Primary.	Secondary.	Insoluble in dilute acid.
—	8 hours.	1	99	—
NaCl .....	8 "	—	100	—
SiO <sub>2</sub> .....	8 "	1	99	—
CaSO <sub>4</sub> .....	8 "	—	100	—
CaCl <sub>2</sub> .....	8 "	2	98	—
CoCl <sub>2</sub> .....	7 "	62	14	23
CuCl <sub>2</sub> .....	8 "	11	*	50
ZnCl <sub>2</sub> .....	7 "	47	37	16
CoCl <sub>2</sub> .....	8 "	50	20	30
HgCl <sub>2</sub> .....	8 "	20	*	*

\* Not determined.

The temperature in every case varied between 200° and 240° except in the case of *n*-butylaniline, which was heated alone at 240—260°. The experiments are, however, not comparable. When the amine was heated with cupric chloride the mixture at the end of the reaction was very dark and contained small, bright red, metallic particles, presumably of copper. The yield of amines insoluble in dilute hydrochloric acid was also high. In the experiment with mercuric chloride some metallic mercury was obtained.

It was observed that the intramolecular rearrangement of the butylaniline was accompanied by the combination of the secondary amine with the substance added. Some of these additive compounds have been isolated.

*n*-Butylaniline cobaltochloride was obtained by heating butylaniline with an excess of finely powdered anhydrous cobalt chloride in the presence of chloroform. After collecting the excess of suspended metallic salt, the chloroform solution was evaporated to dryness, when the cobaltochloride was obtained as a greenish-blue, vitreous mass, which becomes viscous after heating at 100°. It is decomposed by water with the formation of cobalt chloride and butylaniline:

0.4226 gave 0.4265 AgCl. Cl=25.0.

$C_{10}H_{15}N, CoCl_2$  requires Cl=25.4 per cent.

*n*-Butylaniline zincchloride was obtained as a grey, vitreous mass by heating *n*-butylaniline in chloroform solution with an excess of zinc chloride. The solution was filtered from the zinc chloride and the solvent removed by distillation. On washing with small quantities of light petroleum to remove the excess of butylaniline, the zincchloride remained in a pure condition:

0.1450 gave 0.1458 AgCl. Cl=24.9.

$C_{10}H_{15}N, ZnCl_2$  requires Cl=24.9 per cent.

*n*-Butylaniline and cadmium chloride also form an additive com-

pound, which in common with those of the chlorides of cobalt and zinc is readily decomposed by hot water. The instability of the zincichloride toward water explains the readiness with which primary amines may be separated from secondary by the use of zinc chloride.

Evidence was obtained of the formation of compounds with ferric chloride and cupric chloride by warming the chlorides with a chloroform solution of butylaniline. With ferric chloride a very dark green substance was obtained, soluble in aqueous alcohol (75 per cent.), giving a bright green colour. Cupric chloride gave a deep violet chloroform solution, yielding a solid which was almost black.

With the chlorides of calcium or sodium, or with calcium sulphate and silica, no indications were obtained of the formation of additive compounds.

*Additive Compounds of 4-Amino-n-butylbenzene with  
Metallic Salts.*

The products of intramolecular change apparently contained additive compounds of the primary amine with the salt employed. A few of these compounds were prepared and analysed.

*4-Amino-n-butylbenzene zincichloride* was obtained as a caseous mass by adding an aqueous solution of zinc chloride to 4-amino-n-butylbenzene:

0.2355 gave 0.1540 AgCl. Cl=16.2.

$(C_{10}H_{15}N)_2ZnCl_2$  requires Cl=16.3 per cent.

It is sparingly soluble in water, alcohol, or ether. Dilute acids hydrolyse it rapidly.

*4-Amino-n-butylbenzene cobaltchloride* was prepared by mixing alcoholic solutions of anhydrous cobalt chloride with an excess of the base. After being crystallised from absolute methyl alcohol, it formed a bright blue powder which is decomposed by water into its components, slowly in the cold, but more quickly on warming:

0.0858 gave 0.0562 AgCl. Cl=16.2.

0.2155 „ 0.0793 CoSO<sub>4</sub>. Co=14.0.

$(C_{10}H_{15}N)_2CoCl_2$  requires Cl=16.6; Co=13.8 per cent.

*4-Amino-n-butylbenzene cadmichloride* was obtained as a white, bulky mass by mixing the components in methyl-alcoholic solution. It crystallises from hot methyl alcohol in small, white crystals with a nacreous lustre, and tends to form crusts of crystals on the surface of the solution. It is hydrolysed on boiling with water.

*Action of Heat on n-Butylaniline Hydrochloride.*

Crude mono-*n*-butylaniline was converted into its hydrochloride by evaporating it with an excess of concentrated hydrochloric acid until the solution was of a syrupy consistency. On keeping overnight it had solidified to a hard mass of crystals, which were transferred to a retort and heated in an oil-bath at 260–300°. The disengaged vapours were passed through a condenser to remove any liquid. A considerable amount of a liquid was condensed, nearly all of which boiled between 80° and 83°, indicating the presence of *n*-butyl chloride. The gas which escaped condensation was passed through bromine, and after removing the excess of bromine by means of sodium hydrogen sulphite, a small amount of a colourless liquid was obtained, which was not further examined. In this experiment an excess of hydrochloric acid was originally present. Another experiment was carried out taking precautions to avoid an excess. The hydrochloride was dried on a steam-bath for twelve hours, and exposed to the air for a further period, after which it was heated at 280–300° for one hundred hours. During the earlier stages of the experiment, a liquid (1) was condensed, which became darker as the heating proceeded. The gas evolved was passed through bromine, when a liquid dibromide was obtained in small amount.

From the distillate (1) there separated a small quantity of fat, grey crystals, which consisted of aniline hydrochloride. The liquid portion, after being rendered alkaline, gave, on distillation, a fraction boiling between 70° and 80°, chiefly at 77–80°, which was *n*-butyl chloride. There was also a fraction boiling chiefly between 200° and 250°, containing principally a primary amine mixed with some secondary, the former being identified as aniline.

The residue in the flask, which was black and tarry, was rendered alkaline, and the resulting amine treated with an excess of zinc chloride solution, in order to separate the primary amines from the other products. The insoluble zincchlorides gave a mixture of amines boiling between 200° and 255°, and yielding a considerable fraction at 240–255°. The ethereal washings of the zincchloride contained a secondary amine, boiling between 230° and 250°, whilst at 250–260° a mixture of primary and secondary amines was obtained. There were also present bases which were insoluble in dilute hydrochloric acid, but soluble in the concentrated acid, and were probably diphenylamine derivatives.

*Preparation of n-Butylaniline Hydrochloride.*

*n*-Butylaniline hydrochloride has previously been obtained by Kahn (*Ber.*, 1885, 18, 3361) by evaporating a solution of *n*-butyl-

aniline in hydrochloric acid to crystallisation. A more convenient method was to pass a stream of dry hydrogen chloride into a solution of butylaniline in an equal volume of benzene or toluene. A considerable amount of heat was generated, sufficient to evaporate some of the hydrocarbon. On cooling, *n*-butylaniline hydrochloride crystallised out, and was collected, washed, and dried. The filtrate, which still contained much of the salt, was precipitated by the addition of ether, when the hydrochloride was obtained in very small, white crystals having a silvery appearance. They were collected, washed with further amounts of ether, and dried, first at 60° and later at 100°.

*n*-Butylaniline hydrochloride crystallises in very small, irregular plates from hot ethyl acetate, in which it is readily soluble. It is only moderately soluble in the cold solvent.

*Comparative Experiments on Alkylarylamines with various Alkyl Groups.*

A comparison was made of the stability of alkylarylamines containing alkyl groups of different weight. For this purpose methyl- and *n*-butyl-arylamines were employed. In the earlier investigations the experiments were carried out on the intramolecular rearrangement of methyl- and *n*-butyl-aniline. The secondary amines were heated in sealed tubes with a molecular proportion of substances which aid the formation of aminoalkylbenzenes. The tubes were arranged in iron shields in such a manner that the temperature and the duration of heating were approximately the same in each case. The results are given in the following table. The results show that there is a difference, although not very marked, in the behaviour of the two amines, *n*-butylaniline undergoing intramolecular change more readily. In this case the action is characterised by the formation of appreciable quantities of substances of the nature of diphenylamine, which are either absent in the case of methylaniline or present only in small amount.

Substance added.	Time of heating.	<i>n</i> -Butylaniline.		Methylaniline.	
		Primary. Per cent.	Secondary. Per cent.	Primary. Per cent.	Secondary. Per cent.
CoCl <sub>2</sub> .....	5 hours.	73	10	57	32
CoCl <sub>2</sub> .....	6 "	52	24	43	24
HCl .....	6 "	*	20	—	95
HCl .....	8 "	68	18	23	*
CoCl <sub>2</sub> ( $\frac{1}{2}$ mol.)	5 "	*	33	*	50
HCl .....	4 "	*	33	*	49

\* Not estimated.

It was observed that methylaniline yields additive compounds with cobalt chloride, zinc chloride, and cadmium chloride similar to those described in the case of *n*-butylaniline (p. 126).

*Methylaniline cobaltchloride* was obtained as a dull blue powder on triturating anhydrous cobalt chloride with an excess of freshly distilled methylaniline and heating the mixture on a steam-bath for a short time, the excess of methylaniline being then extracted by means of chloroform. On long keeping, the salt became greenish-yellow:

0.1157 gave 0.1402 AgCl. Cl = 30.0.

0.4312 „ 0.2818 CoSO<sub>4</sub>. Co = 24.9.

C<sub>7</sub>H<sub>7</sub>N<sub>3</sub>CoCl<sub>3</sub> requires Cl = 30.2; Co = 25.1 per cent.

*Methylaniline cadmichloride* was prepared in a similar way. It is a white powder, which is decomposed by water:

0.4099 gave 0.4016 AgCl. Cl = 24.2.

0.3045 „ 0.2150 CdSO<sub>4</sub>. Cd = 39.0.

C<sub>7</sub>H<sub>7</sub>N<sub>3</sub>CdCl<sub>3</sub> requires Cl = 24.6; Cd = 39.0 per cent.

In the formation of the additive compounds of alkylanilines with metallic salts, the steric effects of the alkyl group may affect the formation of the compounds to a different extent, and for this and other reasons (difficulty of ensuring the same temperature and pressure in each tube) the experiments are probably not strictly comparable. The comparison of the relative stability of methyl and *n*-butyl groups was therefore carried out with tertiary amines, such as methyl-*n*-butylaniline. The intramolecular rearrangement of this compound proceeds in two stages, namely, the formation of a secondary amine, followed by conversion into a primary amine. It therefore became necessary to prepare the compounds that may possibly occur in the mixture

#### *Methyl-n-butylaniline.*

This substance was prepared in three ways, namely, by the interaction of (a) *n*-butyl bromide and methylaniline, (b) *n*-butyl chloride and methylaniline, (c) methyl iodide and *n*-butylaniline, and the products in each case were the same. It was found that to obtain pure methyl-*n*-butylaniline by distillation was a tedious operation leading to losses. In the earlier work the process of purification consisted in converting the crude methyl-*n*-butylaniline into its picrate, and then crystallising the picrate until pure. This procedure was abandoned later and the secondary amine was removed by heating the crude tertiary amine with a slight excess of the theoretical amount of phenylcarbimide. The excess of the reagent was removed by warming with water, followed by distillation in a cur-

rent of steam. *Methyl-n-butylaniline* was obtained in this way as a pale yellow, refractive liquid boiling at 242–243°/766 mm.:

0.1071 gave 0.3180 CO<sub>2</sub> and 0.0987 H<sub>2</sub>O. C=81.0; H=10.3.

0.0988 „ 7.7 c.c. N<sub>2</sub> at 28° and 748 mm. N=8.8.

C<sub>11</sub>H<sub>17</sub>N requires C=80.9; H=10.5; N=8.6 per cent.

The *hydrochloride* was obtained as an oil on passing a stream of dry hydrogen chloride into an ethereal solution of the base. After repeated washings with small quantities of dry ether, and keeping over potassium hydroxide under diminished pressure, it solidified to a mass of white, glistening laminae:

0.1633 gave 0.1170 AgCl. Cl=17.7.

C<sub>11</sub>H<sub>17</sub>N.HCl requires Cl=17.8 per cent.

It is extremely soluble in water or alcohol, moderately so in nitrobenzene, and sparingly so in toluene.

From an aqueous solution of the hydrochloride containing a slight excess of free acid, the *platinichloride* was obtained as an orange-yellow precipitate sparingly soluble in water:

0.1152 gave 0.0304 Pt. Pt=26.4.

0.2234 „ 7.0 c.c. N<sub>2</sub> at 18° and 738 mm. N=3.6.

(C<sub>11</sub>H<sub>17</sub>N)<sub>2</sub>.H<sub>2</sub>PtCl<sub>6</sub> requires Pt=26.5; N=3.8 per cent.

The *picrate* crystallises from a methyl-alcoholic solution of the components in small, yellow crystals melting at 90°.

*Titration with Titanous Chloride*.—0.010 required 20.3 c.c. TiCl<sub>3</sub> (1 c.c. TiCl<sub>3</sub>=0.001257 gram Fe). Calc. as C<sub>11</sub>H<sub>17</sub>N, C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>N<sub>3</sub>=100.5 per cent.

The melting point of this compound differs from that recorded by Komatsu (*loc. cit.*), who gives 141–142°. The picrates from the amine obtained by introducing the alkyl groups in different order were found to be identical, and a mixture of them also melted at 90°.

*p-Nitrosomethyl-n-butylaniline*.—Nitrous acid acted on a solution of methyl-n-butylaniline hydrochloride containing free hydrochloric acid yielding a reddish-brown solution, and the addition of ice-cold dilute aqueous ammonia precipitated the base as an oil, which was removed by means of ether. It was obtained as a greenish-blue liquid, which was steel-blue by reflected light:

0.1184 gave 0.2981 CO<sub>2</sub> and 0.0909 H<sub>2</sub>O. C=68.7; H=8.5.

0.1282 „ 16.2 c.c. N<sub>2</sub> at 15° and 745 mm. N=14.8.

C<sub>11</sub>H<sub>16</sub>ON<sub>2</sub> requires C=68.7; H=8.4; N=14.6 per cent.

On heating the base under reflux with an excess of a 10 per cent. aqueous solution of sodium hydroxide, decomposition occurred with the production of a volatile amine, probably methyl-n-butylamine.

*4-Methylamino-n-butylbenzene* was obtained by heating 4-amino-

*n*-butylbenzene with methyl iodide. The addition of a dilute solution of sodium hydroxide liberated the base as an almost colourless oil boiling at 262—265°/760 mm.:

0.1042 gave 7.6 c.c.  $N_2$  at 15° and 759 mm.  $N=8.7$ .

$C_{11}H_{17}N$  requires  $N=8.6$  per cent.

By the action of nitrous acid 4-*n*-butylphenylmethylnitrosoamine,  $C_{11}H_{16}ON_2$ , was obtained as a pale yellow oil. This was nitrated by dissolving it in glacial acetic acid, and cautiously adding ten times its weight of fuming nitric acid in the cold. After a short time the reaction was completed by heating on the water-bath until the mixture was pale red or yellow. This was then poured on crushed ice, and the nitro-derivative collected and crystallised by dissolving it in cold fuming nitric acid. On keeping, dinitro-*n*-butylphenyl-4-methylnitrosoamine,  $C_{11}H_{14}O_6N_4$ , was obtained in pale yellow plates. From warm glacial acetic acid it crystallises in very pale yellow, glistening plates at 86°.

Ethyl-*n*-butylaniline was obtained by the action of *n*-butyl chloride on ethylaniline and also by allowing ethyl iodide to react with butylaniline. It was obtained pure in the manner described for methylbutylaniline, and is a pale yellow oil boiling at 248°/768 mm.:

0.0968 gave 0.2880  $CO_2$  and 0.0891  $H_2O$ .  $C=81.1$ ;  $H=10.2$ .

0.0836 „ 5.9 c.c.  $N_2$  at 25° and 748 mm.  $N=8.0$ .

$C_{12}H_{19}N$  requires  $C=81.3$ ;  $H=10.8$ ;  $N=7.9$  per cent.

The picrate crystallises from aqueous alcohol in bright yellow, thin prisms or narrow plates melting at 100°:

0.010 required 20.0 c.c.  $TiCl_3$  (1 c.c.  $TiCl_3=0.00125$  gram Fe). Calc. for  $C_{12}H_{19}N, C_6H_5O_7N_3=99.3$  per cent.

*p*-Nitrosoethyl-*n*-butylaniline was obtained as an oil having a dark blue, metallic colour when viewed by reflected light:

0.017 gave 12.1 c.c.  $N_2$  at 24° and 741 mm.  $N=13.7$ .

$C_{12}H_{18}ON_2$  requires  $N=13.6$  per cent.

*p*-Nitrosoethyl-*n*-butylaniline zincchloride was prepared by mixing alcoholic solutions of the components and evaporating the alcohol under diminished pressure, but it was not obtained crystalline.

4-Ethylamino-*n*-butylbenzene is a liquid of agreeable odour and boiling at 270—272°/762 mm.:

0.1024 gave 7.5 c.c.  $N_2$  at 22° and 746 mm.  $N=8.2$ .

$C_{12}H_{19}N$  requires  $N=7.9$  per cent.

The nitrosoamine is a yellow oil:

0.0999 gave 11.65 c.c.  $N_2$  at 20° and 746 mm.  $N=13.4$ .

$C_{12}H_{18}ON_2$  requires  $N=13.6$  per cent.

*2-Amino-5-n-butyltoluene.*

Molecular proportions of *n*-butyl alcohol and *o*-toluidine were heated at 200–240° for twenty-four hours, and the mixture was treated in the manner already described for 4-amino-*n*-butylbenzene. 2-Amino-5-*n*-butyltoluene was obtained as a very pale yellow liquid boiling at 265–268°/765 mm.:

0.0960 gave 7.1 c.c. N<sub>2</sub> at 20° and 757 mm. N=8.6.

C<sub>11</sub>H<sub>17</sub>N requires N=8.6 per cent.

The hydrochloride crystallises from warm dilute hydrochloric acid in rosettes of white needles:

0.1176 gave 0.0840 AgCl. Cl=17.8.

C<sub>11</sub>H<sub>17</sub>N.HCl requires Cl=17.8 per cent.

It is precipitated from aqueous solution by the addition of an excess of hydrochloric acid.

The acetyl derivative crystallises from dilute aqueous alcohol in white masses of crystals melting at 89°:

0.1039 gave 6.0 c.c. N<sub>2</sub> at 15° and 750 mm. N=6.8.

C<sub>13</sub>H<sub>19</sub>ON requires N=6.8 per cent.

On diazotising the hydrochloride and adding the solution to alkaline β-naphthol, 5-*n*-butyltoluene-2-azo-β-naphthol is precipitated. It crystallises from hot glacial acetic acid in bulky masses of small, bright red needles melting at 105–107°. It is only moderately soluble in alcohol, and dissolves in concentrated sulphuric acid with the production of a purple coloration.

*4-Amino-3-n-butyltoluene.*

This amine was obtained by the action of *n*-butyl alcohol on *p*-toluidine zincchloride, in the manner already described for the preparation of 4-amino-*n*-butylbenzene. It is a liquid boiling at 265–270° under atmospheric pressure:

0.1496 gave 11.3 c.c. N<sub>2</sub> at 19° and 762 mm. N=8.9.

C<sub>11</sub>H<sub>17</sub>N requires N=8.6 per cent.

The acetyl derivative separates as a white mass on cooling the product of interaction of 4-amino-3-*n*-butyltoluene and acetic anhydride. It crystallises from alcohol in tufts of white, slender needles melting at 129°:

0.1113 gave 0.3105 CO<sub>2</sub> and 0.0953 H<sub>2</sub>O. C=76.1; H=9.5.

C<sub>13</sub>H<sub>19</sub>ON requires C=76.0; H=9.3 per cent.



*The Intramolecular Rearrangement of Methyl-*n*-butylaniline.*

Pure methyl-*n*-butylaniline was heated in a sealed tube with one molecular proportion of either zinc chloride or cobalt chloride. In one experiment methyl-*n*-butylaniline hydrochloride was employed. The temperature varied between 200° and 250°, and the heating was allowed to continue for about six to eight hours. On opening the tubes there was usually a pressure due to the presence of an inflammable gas. The contents of the tube were rendered alkaline, and the amines were obtained by distillation in a current of steam. The mixture of amines obtained in this way was treated with zinc chloride solution, which removed the bulk of the primary amines. The ethereal washings of the zincchloride were washed with dilute hydrochloric acid to remove primary, secondary, and tertiary amines. From this acid solution the secondary amines were separated as nitrosoamines and the primary amines converted into the corresponding diazonium salts.

The nitrosoamines separated in this way were nitrated, yielding in each case an oily product, which was obtained crystalline only on keeping in contact with concentrated nitric acid for several days. By pressing on a porous tile to remove oily impurities, and by repeated recrystallisation from glacial acetic acid, a small amount of a pale yellow, crystalline substance was obtained melting at 93°, and the melting point was raised to 94—95° by the addition of 3:5-dinitro-*p*-tolyl-*n*-butylnitroamine. It is probable that the latter compound was present in the nitration product, indicating the existence of *n*-butyl-*p*-toluidine in the mixture of amines from the intramolecular rearrangement of methyl-*n*-butylaniline. It was not found possible to isolate any other nitro-compound in a pure state from the mixture, although appreciable amounts were present.

It is probable that in the mixture dinitro-*n*-butylphenylmethyl-nitroamine was also present, as only *n*-butyl-*p*-toluidine and 4-methyl-amino-*n*-butylbenzene would be expected to occur in any appreciable amount.

In one case small amounts of 2:4:6-trinitrophenylmethyl-nitroamine were isolated, and the primary amine from it indicated *p*-toluidine. By crystallisation of the azo-compounds from this experiment, *p*-tolueneazo- $\beta$ -naphthol, melting at 129°, was isolated, and this melting point was not depressed by the addition of pure *p*-tolueneazo- $\beta$ -naphthol. The small amounts of derivatives of methylaniline and *p*-toluidine isolated were due probably to the rearrangement not proceeding to completion.

*Action of Heat on Methyl-n-butylaniline Hydrochloride.*

Methyl-n-butylaniline (4.2 grams) was dissolved in an excess of concentrated hydrochloric acid in a small glass retort, which was heated in an oil-bath at 150–200°, a stream of hydrogen chloride being allowed to pass through the retort during the period of heating. A portion of the residue in the vessel was removed, and after diluting and adding more hydrochloric acid it was cooled to 0° and treated with a slight excess of an aqueous solution of sodium nitrite. A nitrosoamine separated, which was removed by extraction with ether. The ethereal solution was washed several times with water and dilute sodium hydroxide, dried, and evaporated, and the residue was dissolved in glacial acetic acid, nitrated by heating it on a water-bath with fuming nitric acid, until the colour of the mixture had changed to a pale red. On pouring the mixture into water an oily product was obtained which, when crystallised from fuming nitric acid, melted at 90–92°. The addition of trinitrophenylbutylnitroamine (m. p. 99°) depressed the melting point to about 89–92°, whilst the addition of trinitrophenylmethylnitroamine raised the melting point to 110–115°. The secondary amine resulting from the elimination of alkyl groups from methylbutylaniline in a stream of hydrogen chloride is therefore probably a mixture of methyl- and butyl-aniline.

The further examination of the products of this reaction is deferred until the physical constants of mixtures of trinitrophenylmethylnitroamine and trinitrophenylbutylnitroamine have been determined.

*The Nitration of Dialkylanilines.*

The method usually adopted to nitrate dissimilarly substituted dialkylanilines was to add cautiously about 10 to 15 times their weight of fuming nitric acid to a solution in glacial acetic acid. The reaction was completed by heating on the water-bath until the dark colour of the mixture had given place to a pale yellow or red. The nitration product was then isolated by pouring on ice, when it was collected and purified by crystallisation from fuming nitric acid.

Dibutylaniline, when treated in this way, gave *trinitrophenyl-n-butyl*nitroamine in very pale yellow plates melting at 100°:

0.1093 gave 20.3 c.c.  $N_2$  at 20° and 748 mm.  $N = 21.3$ .

$C_{16}H_{17}O_8N_5$  requires  $N = 21.3$  per cent.

It is soluble in alcohol or acetone, and can be conveniently recrystallised from hot glacial acetic acid. An alcoholic solution of

sodium hydroxide in the cold gives a deep orange-red coloration. It dissolves in cold concentrated sulphuric acid without any development of colour, but on dilution a yellow turbidity is produced.

This substance was shown to be identical with the nitro-derivative obtained on nitrating phenyl-*n*-butylnitrosoamine. It was also obtained by nitrating dibutylaniline in the presence of nitric and sulphuric acids. Dibutylaniline (10 grams) dissolved in concentrated sulphuric acid (18 grams) was slowly added to a mixture of sulphuric (50 grams) and nitric acids (150 grams), the temperature being maintained between 35° and 45° throughout the reaction. After all the amine had been added the mixture was maintained for some time at 50°, and then thrown on crushed ice, when the nitro-compound was collected as a viscous, red substance and purified in the usual manner by crystallisation from fuming nitric acid. The strongly acid aqueous portion was found to contain butyric acid. The nitro-compound was removed by filtration through a thick layer of glass-wool. It was found necessary to take these precautions to remove the last traces of the nitro-compound in order to prevent contamination of the products at a later stage. To the acid filtrate, iron filings were added gradually, care being taken to avoid a too-vigorous action. After remaining overnight, the solution was distilled in a current of steam. The distillate, which still contained a small amount of nitric acid, was neutralised and evaporated to a small bulk. It was then rendered acid by adding an excess of sulphuric acid, and the last traces of nitric acid were removed by a further treatment with iron filings. A further distillation in a current of steam gave a distillate which contained a volatile acid, and this was identified by means of its "distillation constant" determined in an apparatus described by the authors (*Sci. Proc. Roy. Dubl. Soc.*, 1919, **15**, 513). The constant agreed with that for *n*-butyric acid mixed with a small proportion of an impurity, and its presence was confirmed by its odour and by its reaction with ferric chloride.

Comparative experiments were also carried out, using dimethylaniline. Methyl-*n*-butylaniline was nitrated by fuming nitric acid dissolved in glacial acetic acid following the method described above. The product melted at 123–125° after crystallisation from fuming nitric acid. It was recrystallised from glacial acetic acid, and was found to be identical with 2:4:6-trinitrophenylmethylnitroamine, for no depression of the melting point occurred when a mixture was prepared with this nitro-compound and trinitrophenylmethylnitroamine from another source.

Ethyl-*n*-butylaniline, on nitration with fuming nitric acid or with

a mixture of nitric and sulphuric acids, gave a product which, on crystallisation from fuming nitric acid, furnished a mixture yielding trinitrophenyl-*n*-butylnitroamine on crystallisation from glacial acetic acid.

[Received, November 4th, 1919.]

## XVI.—The Condensation of Ethyl Acetoacetate with *p*-Dimethylaminobenzaldehyde and Ammonia.

By LEONARD ERIC HINKEL and HERBERT WILLIAM CREMER.

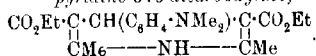
THIS work was interrupted by the war, and as there seems no possibility of it being continued jointly, it was considered advisable to place on record such results as were obtained. The investigation arose from a desire to study the influence of substituent groups in aliphatic and aromatic aldehydes in Hantzsch's pyridine condensation. It was thought that the introduction of basic groups would retard it, and for this purpose *p*-dimethylaminobenzaldehyde was chosen.

The condensation was found to take place very slowly even on heating, the best results being obtained by allowing the mixture to remain for about one hour at the ordinary temperature and then heating under pressure for seven to nine hours. The yield of the dihydro-derivative could not be increased by longer heating or by employing excess of ammonia. The viscous filtrate from the dihydro-compound was subjected to steam distillation, but no aldehyde passed over with the steam. The filtrate was soluble in hydrochloric acid and reprecipitated unchanged by alkali. In all probability, the filtrate contained a *cyclo*-ketone formed by the further condensation of the 1:5-diketone first produced along with the dihydro-compound. The filtrate was not further examined. The dihydro-derivative can also be produced by condensing the aldehyde with ethyl acetoacetate (1 mol.) and ethyl  $\beta$ -amino-crotonate (1 mol.). This method was also employed with *p*-dimethylaminobenzaldehyde, and also, for comparison, with benzaldehyde. In the first case, the yield was 21.7 per cent., whilst with benzaldehyde it was more than 90 per cent., showing in a striking manner the effect of the *p*-dimethylamino-group on the condensation. The oxidation of the dihydro-derivative could not be carried out according to the usual method by nitrous fumes. Even at low temperatures, brown, needle-shaped crystals readily

formed, which were found to be *p*-nitrosodimethylaniline nitrate. The readiness with which the *p*-dimethylaminophenyl group is eliminated is probably due to the influence exerted by the dimethylamino-group, since it has been shown (Schiff and Puliti, *Ber.*, 1883, 16, 160; Epstein, *Annalen*, 1885, 231, 1) that phenyl- and styryl-dimethyldihydropyridinedicarboxylic esters are readily oxidised by nitrous fumes without elimination of the phenyl or styryl groups.

## EXPERIMENTAL.

*Ethyl 4-p-Dimethylaminophenyl-2:6-dimethyl-1:4-dihydro-pyridine-3:5-dicarboxylate,*



A mixture of 30 grams (1 mol.) of *p*-dimethylaminobenzaldehyde, 52 grams (2 mols.) of ethyl acetoacetate, 3.4 grams (1 mol.) of ammonia, and 70 c.c. of alcohol, contained in a closed flask, was allowed to remain for an hour and then heated for nine hours over a rapidly boiling water-bath. Considerable pressure was developed in the flask, which was therefore suitably protected against explosion. On cooling, about half of the contents of the flask crystallised, and the crystals were collected and washed with a small quantity of alcohol. The residue was evaporated over a water-bath until viscid, and, when cold, diluted with an equal volume of alcohol; on stirring, a small, further quantity was obtained, the total yield being 40 grams, or 53.7 per cent. of the theoretical. The crude, yellow crystals were purified by crystallisations from alcohol, acetone, and ethyl acetate, and were obtained finally in nearly colourless, fine needles melting at 158.5°:

0.2452 gave 0.6047 CO<sub>2</sub> and 0.1702 H<sub>2</sub>O. C = 67.26; H = 7.7.

0.1617 „ 10.8 c.c. N<sub>2</sub> (moist) at 7.5° and 750 mm. N = 8.0.

C<sub>21</sub>H<sub>25</sub>O<sub>4</sub>N<sub>2</sub> requires C = 67.64; H = 7.52; N = 7.52 per cent.

The ester is very similar to the trimethyl ester prepared by Hantzsch. It is stable to boiling dilute alkali, and boiling alcoholic potassium hydroxide slowly acts on it, bringing about complete decomposition. When heated with concentrated hydrochloric, sulphuric, or phosphoric acid, the compound is also decomposed, with the elimination of two molecular proportions of carbon dioxide. By virtue of the dimethylamino-group, however, it possesses basic properties and readily forms sparingly soluble additive compounds with hydrogen chloride and with methyl iodide.

*Condensation of p-Dimethylaminobenzaldehyde, Ethyl Acetoacetate, and Ethyl  $\beta$ -Aminocrotonate.*

A mixture of 6 grams (1 mol.) of *p*-dimethylaminobenzaldehyde, 5.2 grams (1 mol.) of ethyl acetoacetate, and 4.5 grams (1 mol.) of ethyl  $\beta$ -aminocrotonate was heated at  $120^\circ$  for several hours. After two days, the viscous mass was dissolved in an equal volume of hot alcohol and left to crystallise. The product, after recrystallisation from ethyl acetate, was identical with the ester just described, the yield being 3.2 grams, or 21.7 per cent. of the theoretical.

The *hydrochloride*,  $C_{21}H_{28}O_4N_2.HCl$ , prepared by dissolving the substance in dilute hydrochloric acid, separates as a fine, white, crystalline powder, especially on dilution with water. It was washed with water and alcohol, and dried in a vacuum:

0.1827 gave 0.4130  $CO_2$  and 0.1257  $H_2O$ .  $C=61.6$ ;  $H=7.63$ .

0.1613 „ 9.4 c.c.  $N_2$  (moist) at  $14^\circ$  and 751 mm.  $N=6.85$ .

0.1466 „ 0.0527  $AgCl$ .  $Cl=8.60$ .

$C_{21}H_{28}O_4N_2.HCl$  requires  $C=61.68$ ;  $H=7.09$ ;  $N=6.85$ ;  $Cl=8.68$  per cent.

It melts at  $201^\circ$ , and, when heated above its melting point, rapidly decomposes, yielding dimethylaniline among the products.

*Methiodide*,  $C_{21}H_{28}O_4N_2.CH_3I$ .—A mixture of the substance with excess of methyl iodide in acetone solution was gently heated for a short time over a water-bath. The clear, hot liquid was then poured into an evaporating basin and stirred with a glass rod until the mass solidified. The crude methiodide was washed with acetone and purified by crystallisation from hot acetone, and finally from ethyl acetate. It melts at  $182$ – $183^\circ$ :

0.1532 gave 0.2892  $CO_2$  and 0.897  $H_2O$ .  $C=51.48$ ;  $H=6.50$ .

0.2052 „ 0.0952  $AgI$ .  $I=25.06$ .

$C_{21}H_{28}O_4N_2.CH_3I$  requires  $C=51.36$ ;  $H=6.03$ ;  $I=24.7$  per cent.

*Ethyl 4-p-Dimethylaminophenyl-2:6-dimethylpyridine-dicarboxylate.*

A mixture of 37.3 grams of the dihydro-ester and 3.2 grams of sublimed sulphur was gently heated at  $150^\circ$ . The mixture melted, and hydrogen sulphide was rapidly evolved, the heating being continued until the liquid became clear and free from gas bubbles. When cold, the mass solidified, and was dissolved in boiling alcohol, from which it crystallised on cooling. The crude crystals were freed from any uncombined sulphur by dissolving them in excess

of dilute hydrochloric acid and filtering. The ester was precipitated as a white, flocculent mass from the acid solution by means of sodium carbonate solution. It was washed with water and recrystallised from alcohol, and finally from light petroleum. The yield was almost quantitative. The ester is readily soluble in benzene, ether, chloroform, or hot alcohol, sparingly so in warm light petroleum, and melts at  $124.5^{\circ}$ :

0.1853 gave 7.65 c.c.  $N_2$  (moist) at  $3^{\circ}$  and 778 mm.  $N = 7.65$ .

$C_{21}H_{26}O_4N_2$  requires  $N = 7.57$  per cent.

*Hydrolysis*.—Fifteen grams of the ester were mixed with 30 grams of potassium hydroxide dissolved in 100 c.c. of alcohol, and the mixture was heated to boiling under a reflux condenser for several hours. On cooling, the potassium salt separated out in fine crystals, which were collected and quickly washed with a little absolute alcohol, and dried in a vacuum. A further yield was obtained from the filtrate on concentration. The potassium salt is yellow and very deliquescent in air, changing to a deep yellow mass. It is sparingly soluble in boiling alcohol. The neutral aqueous solution is deep yellow, but the addition of either acid or alkali instantly destroys the colour, which can, however, be restored by the careful neutralisation of the excess of acid or alkali.

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[Received, November 23rd, 1912.]

## XVII.—*Constituents of the Leaves of Helinus ovatus.*

By JOHN AUGUSTUS GOODSON.

*Helinus ovatus*, E. Meyer (Nat. Ord. *Rhamnaceae*), is a climbing shrub indigenous to South Africa, where it is found growing on the borders of woods and thickets. No species of this genus, which, according to Oliver ("Flora of Tropical Africa"), is confined to Africa and India, appears to have been examined previously, although the constituents of the genus *Rhamnus*, from which the order is named, are fairly well known, including as they do such well-known drugs as cascara sagrada and buckthorn.

The results of the present investigation show that *H. ovatus* contains aconitic acid, quercetin, a saponin, and scyllitol. The last-mentioned substance was first isolated from certain plagiostomous fishes, including the spur dogfish, but has since then been

found in a number of plants, such as the acorns of the common oak and the leaves of *Cocos plumosa* and *C. nucifera*.

The occurrence of scyllitol, the second of the two known *meso*-inositols, in these plants is of considerable biological interest in view of the suggestion made by Winterstein, Contardi, and others (compare Posternak, *Compt. rend.*, 1919, **169**, 37) that phytin, which is believed to be the usual organic phosphorus reserve constituent of plants, is a *meso*inositol hexaphosphate.

The material came from Komgha, Cape Province, and was supplied by Mr. I. B. Pole Evans, Chief of the Division of Botany, Union of South Africa, who stated that it is used medicinally by the natives, and is known locally as "soap-plant," since the leaves have the property of yielding a lather when rubbed in the hands with water.

#### *Preliminary Examination.*

The leaves contained 9.5 per cent. of moisture and 9.2 per cent. of ash, of which 20.2 per cent. was potash ( $K_2O$ ), equivalent to 1.8 per cent. in the leaves.

No alkaloid or cyanogenetic glucoside could be detected by the usual reagents.

The finely ground leaves gave the following percentages of extract on exhaustion in a Soxhlet apparatus with solvents in the order named: petroleum (b. p. 35–60°), 2.2; ether, 2.3; chloroform, 2.2; alcohol, 23.0.

#### *Isolation of Ceryl Alcohol.*

The petroleum extract consisted of brown, waxy matter, of which about one-third remained undissolved when digested with ether. This was boiled with alcoholic potassium hydroxide solution to remove traces of oil and wax. The residue left after removal of the alcohol was crystallised from ethyl acetate, and then melted at 78°; a specimen of ceryl alcohol melted at 81° in the same bath, and a mixture of the two at 79°. (Found: C=82.0; H=14.0. Ceryl alcohol,  $C_{26}H_{54}O$  [Henriques, *Ber.*, 1897, **30**, 1415], requires C=81.6; H=14.2 per cent.)

The remaining extracts were systematically examined, with results which showed that the quantity of plant available (650 grams) could best be dealt with by extraction with chloroform to remove wax and resinous matter, and then in succession with alcohol and water.



*Examination of the Alcoholic Extract.*

The bulk of the alcohol was removed, and the resulting syrup set aside for some days, when it deposited a considerable quantity of potassium chloride. The filtrate was poured into about four times its volume of water, and treated successively with lead acetate and basic lead acetate. The lead was removed from the two precipitates and from the filtrate by hydrogen sulphide in the usual manner.

*Isolation of Quercetin.*

The aqueous solution of the material recovered from the lead acetate precipitate contained a considerable amount of tannin. Extraction with ether removed a small quantity of a yellow substance, probably quercetin (see below). The liquor was then acidified with hydrochloric acid, boiled to hydrolyse glucosides, cooled, and again extracted with ether, the extract yielding a yellow substance crystallising in rosettes of needles. This was recrystallised from a mixture of alcohol and chloroform, and then melted at 309°. On acetylation, it formed matted, colourless needles melting at 195°, and this melting point was not depressed when the substance was mixed with penta-acetylquercetin. The yellow colouring matter is therefore quercetin.

The aqueous solution of the material recovered from the basic lead acetate precipitate also contained tannin, and a small amount of yellow colouring matter, which could not be obtained in a crystalline condition.

The filtrate, after removal of the lead as sulphide, was concentrated and extracted with butyl alcohol, which removed a saponin. The latter was purified by solution in water and precipitation with basic lead acetate, the lead precipitate being decomposed with hydrogen sulphide in the usual manner, and the filtrate evaporated to dryness under diminished pressure. The quantity of saponin obtained was so small that no further purification could be effected. The material frothed strongly in aqueous solution, gave no compound with cholesterol in alcoholic solution, did not reduce Fehling's solution, and was not hæmolytic. It was hydrolysed by boiling with dilute hydrochloric acid, the resulting solution yielding a small amount of apparently crystalline sapogenin on extraction with ether. The residual aqueous solution reduced Fehling's solution strongly, but did not give a crystalline phenylosazone.

The aqueous liquid, after extraction with butyl alcohol, was concentrated under diminished pressure and set aside, when a further

quantity of potassium chloride separated. The filtrate yielded *d*-phenylglucosazone on treatment with phenylhydrazine.

*Examination of the Aqueous Extract.*

The aqueous extract was treated successively with lead acetate and basic lead acetate, and the two precipitates were collected.

*Isolation of Aconitic Acid.*

The lead acetate precipitate was suspended in water and decomposed by hydrogen sulphide. The filtrate was concentrated under diminished pressure and extracted with ether, which removed 12.6 grams of a crystalline substance, corresponding with 1.9 per cent. in the leaves.

This, on recrystallisation from water, formed minute prisms melting at  $191^{\circ}$ , and gave all the reactions of aconitic acid, including that described by Taylor (T., 1919, 115, 886). (Found: C=41.3, 41.4; H=3.9, 3.6. Aconitic acid,  $C_6H_6O_6$ , requires C=41.4; H=3.5 per cent.)

*Isolation of Scyllitol.*

The basic lead acetate precipitate was decomposed in the usual manner, and the filtrate concentrated under diminished pressure, when slightly brown crystals separated. Two crops of the crude substance, amounting to 3 grams and corresponding with 0.46 per cent. in the leaves, were obtained. The product was purified by recrystallisation from hot water, from which it separated in anhydrous, monoclinic rhombs. (Found: C=39.7, 40.1; H=6.8, 6.9. Scyllitol,  $C_6H_{12}O_6$ , requires C=40.0; H=6.7 per cent.)

The properties of the substance agreed closely with those recorded for scyllitol (J. Müller, *Ber.*, 1907, 40, 1821, and H. Müller, T., 1907, 91, 1767; 1912, 101, 2383). When recrystallised slowly from cold water, it separated in transparent, hexagonal prisms, which, on removal from the solvent, became opaque and friable owing to loss of water of crystallisation. Crystals freed as rapidly as possible from adhering mother liquor lost, on exposure to air, 24.9 per cent. of water.  $C_6H_{12}O_6 \cdot 3H_2O$  requires  $H_2O=23.1$  per cent.

H. Müller noted this change in crystal habit and transparency, but did not establish the fact that it is due to loss of water of crystallisation (T., 1907, 91, 1772).

When heated, the scyllitol obtained from *H. ovatus* leaves coloured slightly at 300°, darkened considerably at 320°, and melted and effervesced at 353°, as recorded by a mercury thermometer.

J. Müller (*loc. cit.*) gave the solubility of scyllitol in water as about 1 gram in 100 c.c. at 18°; the author finds a solubility of 1.03 grams in 100 grams at 18° for his specimen, whereas H. Müller (*loc. cit.*) gave it as 1.7 grams in 100 c.c. at 15°.

Its identity with scyllitol was confirmed by the preparation of the hexa-acetyl derivative, which melted at 291°. H. Müller (*loc. cit.*) gives 290—291° (corr.). (Found: C=50.1; H=5.6. Hexa-acetylscyllitol,  $C_6H_6(C_2H_3O)_6O_6$ , requires C=50.0; H=5.6 per cent.)

The filtrate from the lead precipitates, after removal of the lead, contained merely inorganic salts.

In conclusion, the author desires to express his warmest thanks to Dr. Henry for his advice and criticism throughout the course of the work.

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## XVIII.—Contributions to the Chemistry of the Terpenes.

### Part XIX. Synthesis of a *m*-Menthadiene from *m*-isocymene.

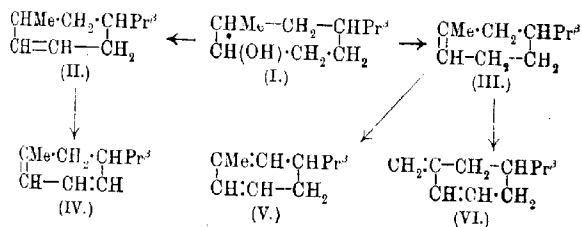
By GEORGE GERALD HENDERSON and THOMAS FREDERICK SMEATON.

SEVERAL menthadienes have been prepared by various synthetic methods, but none that belongs to the meta-series, and may therefore be considered a derivative of *m*-isocymene, had been synthesised until the problem was successfully attacked by W. H. Perkin, jun., and his collaborators (compare T., 1905, **87**, 1083; 1907, **91**, 480; 1908, **93**, 1876; 1910, **97**, 2129; 1911, **99**, 118). Sylvestrene, carvestrene, and the other meta-menthadienes prepared synthetically by these investigators contain one ethylenic linking in the nucleus and one in a side-chain, hence it appeared desirable to obtain a menthadiene of the meta-series containing two ethylenic linkings in the nucleus in order to compare its properties with those of the corresponding para-menthadienes.

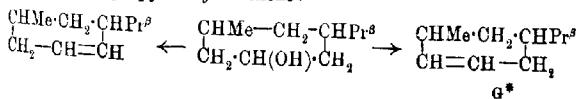
Starting with *m*-isocymene, obtained by the action of phosphoric oxide on fenchone, we first prepared *m*-isocymene-6-sulphonic acid

and converted this into the corresponding phenol, 6-hydroxy-*m*-isocymene, by fusion with alkali. The succeeding steps in the process, which was similar to that previously adopted by one of us for the synthesis of menthadienes from thymol and carvacrol respectively (Henderson and Boyd, T., 1911, **99**, 2159; Henderson and Schotz, T., 1912, **101**, 2563), were briefly as follows: (1) Preparation of *m*-menthan-6-ol (1-methyl-3-isopropylcyclohexan-6-ol),  $C_{10}H_{18} \cdot OH$ , from 6-hydroxy-*m*-isocymene by hydrogenation in the presence of active nickel. (2) Dehydration of the *m*-menthanol by heating with oxalic acid, with the formation of a *m*-menthene (1-methyl-3-isopropylcyclohexene),  $C_{10}H_{18}$ . (3) Preparation of the *m*-menthene dibromide,  $C_{10}H_{16}Br_2$ . (4) Conversion of the dibromide into a *m*-menthadiene (1-methyl-3-isopropylcyclohexadiene),  $C_{10}H_{16}$ , by elimination of two molecular proportions of hydrogen bromide through treatment with alcoholic potassium hydroxide.

It is evident that dehydration of 1-methyl-3-isopropylcyclohexan-6-ol (I) might result in the formation of either 1-methyl-3-isopropyl- $\Delta^3$ -cyclohexene (II) or 1-methyl-3-isopropyl- $\Delta^6$ -cyclohexene (III). The dibromide of the former hydrocarbon would yield on treatment with alcoholic potassium hydroxide 1-methyl-3-isopropyl- $\Delta^{4,6}$ -cyclohexadiene (IV), whilst from the latter either of two isomerides, 1-methyl-3-isopropyl- $\Delta^{1,5}$ -cyclohexadiene (V) or 1-methylene-3-isopropyl- $\Delta^5$ -cyclohexadiene (VI), might be produced in a similar manner.



Direct evidence of the constitution of the hydrocarbon,  $C_{10}H_{18}$ , which we obtained from the *m*-menthanol, is lacking, but its properties are very similar to those of a *m*-menthene which was prepared by Knoevenagel (*Annalen*, 1897, **297**, 169) by heating 1-methyl-3-isopropylcyclohexan-5-ol with phosphoric oxide at 110–130°, and should therefore be either 1-methyl-3-isopropyl- $\Delta^4$ -cyclohexene or 1-methyl-3-isopropyl- $\Delta^5$ -cyclohexene:

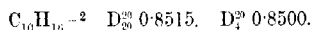


The physical constants of the two hydrocarbons are as follows:

	B. p.	D.	$n_D$	$M_w$
H. and S. ....	167—168°	0.8222	1.45683	45.61
K. ....	167—168°	0.8197	1.45609	45.67

Comparison of the figures suggests the conclusion that the substances are identical, and therefore that the hydrocarbon which we obtained from 1-methyl-3-isopropylcyclohexan-6-ol is 1-methyl-3-isopropyl- $\Delta^5$ -cyclohexene (II). If this is the case, the dibromide prepared from it is 5:6-dibromo-1-methyl-3-isopropylcyclohexane, and therefore the hydrocarbon,  $C_{10}H_{16}$ , which the dibromide yields on treatment with alcoholic potassium hydroxide, is in all probability 1-methyl-3-isopropyl- $\Delta^{1:6}$ -cyclohexadiene (IV). The following evidence in support of this view may also be quoted. Harries and Antoni (*Annalen*, 1903, **328**, 88) obtained a "dihydrocymene,"  $C_{10}H_{16}$ , by distilling the phosphate of 1:3-diamino-*m*-menthane, which should be either  $\Delta^{1:6}$  or  $\Delta^{1:5}$ . 1-methyl-3-isopropylcyclohexadiene. The properties of this hydrocarbon—boiling point 172—174°,  $D_{15}^{25}$  0.8423,  $n_D^{25}$  1.47936—do not correspond at all closely with those of our *m*-menthadiene, which are as follows: boiling point 169—171°,  $D_{20}^{20}$  0.8515,  $n_D^{20}$  1.47270. Apparently, therefore, the latter is not the  $\Delta^{1:5}$ -isomeride, whilst if the *m*-menthene from which it is derived has the  $\Delta^5$ -structure, as appears probable, formula VI is also excluded.

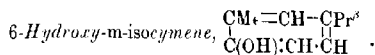
Of the three possible formulæ for the menthadiene, there is none in which conjugated double bonds are absent, and, indeed, the fact that it is not capable of uniting additively with more than one molecular proportion of bromine, although containing two ethylenic linkings in its molecule, shows that it has this conjugated structure. Nevertheless, the value found for its molecular refraction was normal, instead of showing an exaltation, as might have been expected. At the same time, it should not be forgotten that, according to Auwers and Eisenlohr (*Ber.*, 1910, **43**, 80), the presence of conjugated ethylenic linkings in a compound can be established with more certainty from consideration of its molecular



Molecular refraction.				
Line.	$n_D^{20}$	Found.	Calculated.	$\Delta$ .
D .....	1.47270	44.89	45.24	-0.35
C .....	1.46964	44.65	44.97	-0.32
G .....	1.48802	46.21	46.39	-0.18
Molecular dispersion ( $M_w - M_v$ ) .				
		Found.	Calculated.	$\Delta$ .
		1.56	1.426	0.134
				= 9.4 per cent

dispersion than from the molecular refraction, and, as shown in the above table, the figures obtained for the *m*-menthadiene confirm the view expressed regarding its structure.

# EXPERIMENTAL.



*m*-isoCymene (1-methyl-3-isopropylbenzene) was prepared from fenchone by treatment with phosphoric oxide, according to Wallach's method (*Annalen*, 1893, **275**, 158), and converted into 6-hydroxy-*m*-isocymene by the process described by Kelbe (*Annalen*, 1881, **210**, 30), with certain modifications. On warming with concentrated sulphuric acid, *m*-isocymene yielded readily a mixture of *m*-isocymene-6-sulphonic acid and *m*-isocymene-4-sulphonic acid, the latter only in small proportions. The sulphonic acids were converted into their barium salts in the usual way, and the salt of the 4-acid, which is more readily soluble in water, was separated from the sparingly soluble salt of the 6-acid. The potassium salt of the 6-acid was obtained by heating the barium salt with a concentrated aqueous solution of potassium carbonate, and purified by crystallisation from water, from which it separates in lustrous plates. Finally, the potassium salt was fused with six times its weight of potassium hydroxide, the fusion dissolved in water, the solution acidified, and the 6-hydroxy-*m*-isocymene distilled over in a current of steam. From the distillate it was separated, partly by means of a tap funnel and partly by extraction with ether, dried, and distilled (b. p. 231°). It is a colourless, refractive liquid, the vapour of which has a very irritating effect on the lungs.

## 1-Methyl-3-isopropylcyclohexan-6-ol (I).

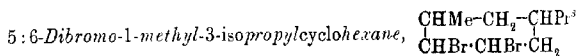
The 6-hydroxy-*m*-isocymene was converted into 1-methyl-3-isopropylcyclohexan-6-ol by treatment with hydrogen in the presence of active nickel. In order to obtain the nickel in an active form, the hydroxide of the metal was precipitated by the addition of potassium hydroxide to a solution of the pure nitrate, the precipitate washed exhaustively with water, formed into a paste by admixture of granules of pumice, and dried. The greater part of a long combustion tube was filled with the mixture, and the oxide of nickel reduced with pure hydrogen at 280°. The 6-hydroxy-*m*-isocymene was placed in a boat in the front part of the tube, which was maintained at 170–180° while a steady stream of carefully

purified hydrogen was passed through. The hydrogenation product distilled slowly into the receiver as a colourless liquid. Attempts to crystallise the compound from various solvents, or by cooling, having proved unsuccessful, it was purified by distillation under diminished pressure.

1-Methyl-3-isopropylcyclohexan-6-ol is a colourless, somewhat viscous liquid with a pleasant odour. It is very sparingly soluble in water and readily so in alcohol or ether. Its physical constants are as follows: boiling point 119—121°/28 mm.,  $D_4^{20}$  0.9156,  $n_D^{20}$  1.46659,  $M_D$  found 47.30, calc. 47.55.

1-Methyl-3-isopropyl- $\Delta^5$ -cyclohexene (II).

In order to effect dehydration, the purified 1-methyl-3-isopropylcyclohexan-6-ol was mixed with about twice its weight of finely powdered anhydrous oxalic acid and boiled for several days in a flask provided with an air condenser until the process appeared to be completed. The contents of the flask were distilled in a current of steam, when a clear, oily liquid passed over and floated on the surface of the aqueous layer. The distillate was saturated with ammonium sulphate and extracted with ether, the ethereal extract washed with water and dried over anhydrous calcium chloride, and the ether removed by distillation. The residual liquid was distilled, and two fractions were collected, the larger one boiling at 165—185° and the other at 185—205°. The latter was set aside for further treatment with oxalic acid, and the fraction which boiled at 165—185° was redistilled over sodium until a product of constant boiling point was obtained. 1-Methyl-3-isopropyl- $\Delta^5$ -cyclohexene is a colourless, mobile liquid with an agreeable odour. Its boiling point is 167—168°/760 mm.,  $D_4^{20}$  0.8222,  $n_D^{20}$  1.45683,  $M_D$  found 45.61, calc. for  $C_{10}H_{18}$  45.39. It is unsaturated, immediately decolorising solutions of potassium permanganate and of bromine.



A cooled solution of bromine (1 mol.) in glacial acetic acid was added gradually to a solution of the *m*-menthene (1 mol.) in the same solvent, cooled with ice-water, and stirred continuously. After addition of the bromine, the solution was left for half an hour and then poured into ice-water. The dibromo-derivative settled down as a heavy, oily liquid, almost colourless, which was washed with water until free from acetic acid, and used for the next operation without further purification

*1-Methyl-3-isopropyl- $\Delta^{4:6}$ -cyclohexadiene (IV).*

The dibromo-derivative was boiled for several hours under a reflux condenser with an excess of alcoholic potassium hydroxide until no further separation of potassium bromide took place. The mixture was then distilled in a current of steam, and the oily distillate separated from the water with the aid of light petroleum. The extract was washed with water and dried over anhydrous potassium carbonate, and the petroleum then distilled off. The liquid which remained was fractionally distilled over sodium in an atmosphere of dry hydrogen; no signs of decomposition were observed during the process, and the distillate was perfectly colourless. After several fractionations, a product of constant boiling point was obtained.

*1-Methyl-3-isopropyl- $\Delta^{4:6}$ -cyclohexadiene* ( $\Delta^{4:6}$ -*m*-menthadiene) is a colourless, limpid liquid with an agreeable odour. It boils at  $169-171^{\circ}/760$  mm., and has  $D_4^{20}$  0.8515,  $n_D^{20}$  1.47270,  $M_D$  found 44.89, calc. for  $C_{10}H_{16}$  45.24. The hydrocarbon is unsaturated, at once reducing an alkaline solution of potassium permanganate, but is not capable of combining additively with more than one molecular proportion of bromine. With sulphuric acid, it gives a red, with sulphuric acid and alcohol a reddish-brown, and with acetic anhydride and sulphuric acid a violet, coloration. From the results of the determination of its physical constants, shortly after purification and again after an interval of seven days, it evidently undergoes change, probably polymerisation, on keeping. Thus the following results were obtained with a specimen which had been set aside for a week after purification:  $D_4^{20}$  0.8614,  $n_D^{20}$  1.47437,  $M_D$  found 44.44. The *m*-menthadiene appears, in fact, to behave in a similar way to cyclopentadiene (compare Auwers and Eisenlohr, *loc. cit.*).

We take this opportunity of expressing our gratitude to Mr. W. G. Birrell for valuable assistance in the experimental part of the work, and to the Research Fund Committee of the Carnegie Trust for a grant in aid of the expenses.

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XIX.—*The Effect of a Change in Temperature on the Colour Changes of Methyl-orange and on the Accuracy of Titrations.*

By HENRY THOMAS TIZARD and JOHN REGINALD HARVEY WHISTON.

IN a former paper (T., 1910, **97**, 2477), one of us gave the results of quantitative measurements of the depth of colour of solutions of methyl-orange containing varying concentrations of hydrogen ions. The results could be quantitatively accounted for on the simple theory that methyl-orange was a (pseudo-) acid of a strength of about  $4.2 \times 10^{-4}$  at about  $25^\circ$ , and that the depth of colour of the red (undissociated) form of the acid was 18.8 times that of the yellow dissociated form or acidic ion in solutions of the same strength. The calculation of the dissociation constant depends directly on the latter measurement, for (see previous paper) if  $\alpha$  is the degree of dissociation of the indicator acid and  $C_0$  the depth of colour of the undissociated molecule compared to that of the dissociated molecule as unity, the colour of a solution containing a fraction  $\alpha$  of the acid in the dissociated form is:

$$C = C_0(1 - \alpha) + \alpha \quad \dots \dots \dots (1)$$

and the concentration of the hydrons in the solution is given by

$$C_H = K \cdot \frac{1 - \alpha}{\alpha} \quad \dots \dots \dots (2)$$

If  $C_0$  and  $C$  are measured,  $\alpha$  can be calculated from (1) and  $K$  from (2). A mistake in the value of  $C_0$  of course alters the calculated value of  $K$ .

The results recorded in the present paper agree at  $25^\circ$  very well with the older measurements in not too acid solutions. When more acid is present, they are consistently lower. This may be partly due to the fact that a different sample of methyl-orange was used, but it is more likely that the depth of colour in the more strongly acid (red) solutions was previously overestimated. This would mean that the value of  $K$  at  $25^\circ$ , calculated in the previous paper, was too high; present measurements give  $3.8 \times 10^{-4}$  at  $25^\circ$  instead of  $4.25 \times 10^{-4}$ . It is, naturally, difficult to compare accurately the depths of colour of solutions which differ in tint, even though the difference is very slight, as in the present case.

The determination of the concentration of hydrons in aqueous solutions by means of "indicators" has been frequently used during

the last few years. It has been generally assumed that the effect of temperature on the depth of colour of solutions containing methyl-orange was practically negligible. It was pointed out, however, in a paper read before the British Association in 1912 that this was probably not the case. There seems very little doubt that indicators in general use are pseudo-acids or bases. Now, the strength of pseudo-acids usually increases considerably with the temperature; in other words, their dissociation constants have a very high temperature-coefficient. The sensitiveness of an indicator depends, however, directly on its dissociation constant; if the constant increases, the indicator will become less sensitive to hydriions, and therefore the depth of colour in a solution of any definite hydriion concentration (within the range of sensitiveness) will diminish. A qualitative experiment showing this effect is as follows: if an  $N/200$ -solution of acetic acid containing methyl-orange is heated, the colour of the solution will change from orange to yellow, and increase again on cooling.

Since no quantitative experiments have been made on the effect of temperature on the changes of indicators, it was thought advisable to determine the depth of colour of methyl-orange in solutions of varying acidity at three different temperatures. The measurements were carried out exactly as before with a modified Donnan colorimeter constructed by Köhler in Leipzig. The colorimeter tubes were jacketed outside with tubes, through which a stream of water could be passed. The temperature of the solutions in the colorimeter tubes was thus kept constant by siphoning water through the jacketed tubes from a reservoir kept at the desired temperature. The temperature inside the tubes was (at the higher temperatures) a few degrees lower than that of the bath, but could easily be kept constant within  $1^\circ$  during the series of experiments.

The solutions of varying hydriion concentration were made by mixing known quantities of equivalent solutions of ammonia and acetic acid. These two substances are of practically the same strength, and, further, their strength, and especially that of acetic acid, alters only slightly with the temperature, as the following numbers taken from Lundén's tables show:

	$18^\circ$	$25^\circ$	$40^\circ$
Ammonia .....	1.4	1.77	$1.87 \times 10^{-5}$
Acetic acid .....	1.82	1.86	$1.81 \times 10^{-5}$

Now if we add  $z$  c.c. of ammonia to (say) 10 c.c. of an equivalent solution of acetic acid, then if  $z$  is less than 10, we have a solution containing  $(10-z)$  equivalents of acid and  $z$  equivalents of salt (ammonium acetate), which may be considered to be completely

dissociated in dilute solutions. Then if  $V$  is the (unknown) dilution, the concentration of hydriions is given by

$$K_a \times (\text{concentration of acetic acid}) = (\text{concentration of acetion}) \times (\text{concentration of hydriion}).$$

Hence

$$C_H = \frac{K_a \times (10 - z)}{z} = \frac{1.8 \times 10^{-5} (10 - z)}{z},$$

and is independent of  $V$ , provided this is neither too small nor too large, and also of the temperature, since  $K_a$  alters so little with the temperature. This is by far the easiest way of preparing solutions of any definite concentration of hydriions between  $10^{-3}$  and  $10^{-7}$  (the neutral point).

It is not necessary to know the strengths of the acid and alkaline solutions absolutely so long as their relative strengths are known accurately. For this purpose, it is best to titrate the acid solution directly against standard baryta, using phenolphthalein as indicator, and the ammonia solution, using methyl-red as indicator, against a solution of hydrochloric acid which itself has been titrated against the same baryta solution.

The effect of temperature on the "end-colours" of methyl-orange, that is, on the depth of colour in highly acid and in neutral or alkaline solutions ( $C_H < 10^{-7}$ ), is practically zero. No difference in the depth of colour of the red acid form could be detected when the temperature ranged from  $10^\circ$  to  $40^\circ$ ; this means that whatever is the form of the undissociated acid which imparts the distinctive red colour to the solution, its concentration is altered very little with rise of temperature. The depth of colour of the yellow (alkaline) solution, which one may suppose to contain only the ion,  $N(CH_3)_3 \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot SO_3'$ , appeared to increase slightly when the temperature was raised from  $10^\circ$  to  $40^\circ$ , but the increase is within the unavoidable errors of measurement at these temperatures. The mean of many experiments gave 17.5 as the molecular colour of the undissociated acid, taking that of the yellow dissociated form as unity.

The depths of colour of solutions containing concentrations of hydriions within the limits of sensitiveness are given in the following tables; from the results, the following values for the (apparent) dissociation constant of the indicator were obtained:

Temperature.....	15°	24°	37°
$K$ .....	2.7	3.7	$5.2 \times 10^{-4}$

The values for the depth of colour in the various solutions, calculated from these numbers, are given in the third column of the

tables. The results previously obtained for 25° are included in the table for 24°. The agreement is very satisfactory, except in the more acid solutions; it should be remembered that the former results were all obtained in dilute solutions of hydrochloric acid.

Temperature, 15°;  $K = 2.7 \times 10^{-4}$ ;  $C_0 = 17.5$ .

Concentration of hydriions.	Colour (observed).	Colour (calculated).
$1.3 \times 10^{-5}$ .....	1.10	1.12
5.9 " .....	1.33	1.35
$2.8 \times 10^{-5}$ .....	2.57	2.55
7.0 " .....	4.45	4.38
$1.6 \times 10^{-4}$ .....	7.00	7.14
3.34 " .....	10.0	10.1
5.0 " .....	11.7	11.7
$1.0 \times 10^{-3}$ .....	14.3	14.0
2.0 " .....	15.3	15.5
3.7 " .....	16.0	16.4
$1.0 \times 10^{-2}$ .....	17.1	17.1
$1.0 \times 10^{-1}$ .....	17.8	17.5

Temperature, 24°;  $K = 3.7 \times 10^{-4}$ ;  $C_0 = 17.5$ .

Concentration of hydriion.	Colour (observed).	Colour (calculated).	Previous measurements at 25°.*
$0.16 \times 10^{-4}$ .....	1.66	1.68	1.65
0.365 " .....	2.50	2.48	2.41
0.91 " .....	4.28	4.25	4.13
2.15 " .....	7.10	7.06	7.03
5.0 " .....	10.4	10.5	10.6
$3.7 \times 10^{-3}$ .....	15.7	16.0	—
$10^{-1}$ (N/10-HCl)	17.4	17.5	18.3

\* T., 1910, 97, 2477.

Temperature, 37°;  $K = 5.2 \times 10^{-4}$ ;  $C_0 = 17.5$ .

Concentration of hydriion.	Colour (observed).	Colour (calculated).
$0.28 \times 10^{-4}$ .....	1.90	1.84
0.535 " .....	2.61	2.54
1.58 " .....	4.54	4.84
2.15 " .....	5.60	5.82
5.0 " .....	9.20	9.10
$1.0 \times 10^{-3}$ .....	11.6	11.4
2.0 " .....	14.0	14.1
3.7 " .....	15.4	15.5
$1.0 \times 10^{-2}$ .....	16.3	16.7
$10^{-1}$ .....	17.5	17.4

In the diagram, depths of colour are plotted against concentration of hydriions. The three curves represent the results at the three temperatures chosen; it will be seen that the effect of raising the temperature is to shift the colour curve to the left. The dissociation constant increases linearly with the temperature; extra-

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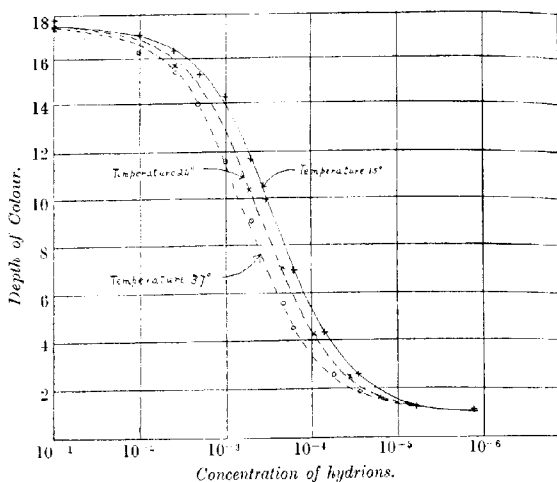
polution gives the following values for the temperatures 10°, 25°, and 40°:

Temperature .....	10°	25°	40°
Dissociation constant	2.1	3.8	$5.5 \times 10^{-4}$

It can be easily shown (see equation 2) from these results that the concentration of hydrion necessary to produce any definite depth of colour is doubled by raising the temperature from 15° to 40°.

## Discussion of Results.

The very great temperature-coefficient of the dissociation constant of methyl-orange may be taken as strong evidence of the truth of



the modern theory that this indicator is a pseudo-acid. No other case in the literature of the subject can be found of an acid of this order of strength ( $K=10^{-4}$ ) increasing in strength appreciably within these limits of temperature. At the same time, it is necessary to reconcile this conclusion with the fact that the red colour of the undissociated acid form of the indicator does not change in depth when the temperature is altered. The obvious explanation of the high temperature-coefficient of the dissociation constant of pseudo-acids is that the equilibrium between the pseudo- and true acid forms of the acid, which we may express by the formula



alters considerably with the temperature. If this is true of methyl-orange, why does not the colour alter? The following seems to be a satisfactory explanation of this difficulty. Methyl-orange, or rather helianthin, is a sulphonic acid. If it were not a pseudo-acid we should therefore expect it to be a strong acid, comparable with sulphuric acid, with a dissociation constant of about 1. Assuming this, we may say that since its dissociation constant is actually found to be of the order  $3 \times 10^{-4}$  (at the ordinary temperature), then the undissociated form of the acid must be an equilibrium mixture consisting almost entirely of the red pseudo-form (or forms) HIXO, whilst only a fraction,  $3 \times 10^{-4}$ , of it is in the yellow, "true acid form" HIOX. Increase in temperature to  $40^\circ$  means that this fraction is increased to  $5.5 \times 10^{-4}$ , without appreciably altering the proportion in the pseudo-acid form. Hence the colour remains practically unchanged.

Since the depth of colour of methyl-orange in a solution containing an  $N/5000$ -concentration of hydrogen ions ( $C_H = 10^{-3.7}$ ) is 5.45 at  $40^\circ$  and 9.1 at  $10^\circ$ —an increase of 65 per cent. for a fall in temperature of  $30^\circ$ —it is clear that if the methyl-orange method is employed for determining quantitatively the concentration of hydriions in a solution, it is important to keep the temperature constant during the measurements. The effect of a change in temperature on the accuracy of an ordinary titration is, however, only very slight. The concentration of hydrogen ions in a solution of a salt made up of a weak base and strong acid is approximately

$$\sqrt{\frac{K_w}{K_b V}}$$

where  $K_w$  and  $K_b$  are the dissociation constants of water and the base respectively, and  $\frac{1}{V}$  is the concentration of the salt in mols. per litre.

The effect of the increase of the dissociation constant of methyl-orange with the temperature is that the concentration of hydriions "indicated" is greater the higher the temperature. Since, however,  $\sqrt{\frac{K_w}{K_b}}$  also increases with the temperature, the two effects tend

to cancel each other, and the accuracy of the titration is not impaired. Taking collidine ( $K_b = 1.6 \times 10^{-7}$  at  $18^\circ$  and  $3 \times 10^{-7}$  at  $40^\circ$ ) as an example of a base for the titration of which methyl-orange is a suitable indicator, the concentration of hydriions at the "equivalent" point, if  $F=20$ , is  $4 \times 10^{-5}$  at  $18^\circ$  and  $7 \times 10^{-5}$  at  $40^\circ$ . The dissociation constant of methyl-orange increases from

$3 \times 10^{-4}$  to  $5.5 \times 10^{-4}$  for this range of temperature, and the depth of colour of methyl-orange in solutions of the above concentration would be 3.0 at  $18^\circ$  and 2.8 at  $40^\circ$  respectively, a difference which is, of course, negligible. The accuracy of a titration in such cases depends mainly on quite other factors, chief of which is the effect of a small excess of acid or base on the hydrolysis of the salt, and this depends only on the strength of the acid or base in question, and not at all on the indicator. In other words, a change in temperature, within reasonable limits, can never necessitate a change of indicator.

We are much indebted to the Research Fund Committee of the Chemical Society for a grant which partly defrayed the cost of the colorimeter.

OXFORD.

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## XX.—*The Rate of Decomposition of Malonic Acid.*

By CYRIL NORMAN HINSHELWOOD.

THE experiments described in this paper were carried out with the object of obtaining information bearing upon recent views on chemical reactivity. The view of Marcellin and of Rice, that a molecule reacts when its energy exceeds the mean energy corresponding with the temperature of the system, was coupled by Lewis (T., 1916, 109, 796) with the hypothesis that the rate of a unimolecular reaction is proportional to the density of infra-red radiation of the frequency absorbable by the system. By introducing a term derived from Planck's equation into the ordinary mass-action equation, Lewis obtained  $E = Nh\nu$ , where  $E/N$  = critical increment for one single molecule,  $h$  = Planck's constant, and  $\nu$  = the frequency of the absorbed infra-red radiation. A detailed account of the radiation theory is given by Perrin (*Ann. Phys.*, 1919, [ix], 11, 5).

In connexion with Rice's view, it is interesting to make measurements of the rate of unimolecular reaction in a system the energy content of which can be varied at constant temperature, for example, to compare the reactivity of a solid system with that of the supercooled liquid at the same temperature. If, moreover, a marked difference in reactivity is found between the two systems, the radiation hypothesis would lead one to expect a difference in their infra-red properties. Naturally, a unimolecular reaction

must be selected for investigation, in order that heterogeneity may not complicate the problem.

Malonic acid was chosen for experiment, since at moderately high temperatures it undergoes a unimolecular decomposition into volatile products, namely, carbon dioxide and acetic acid. The first part of the work was to measure the rate of decomposition of molten malonic acid above its melting point and the supercooled liquid below the melting point, and to compare the values of the velocity constant  $k$  for the supercooled liquid with the corresponding values for the solid. If a large difference existed, it would be worth while looking for a difference in the infra-red properties of the acid in the two states. Actually, a well-marked difference is found in the rates, as the results will show.

The rate of decomposition of malonic acid was measured in glacial acetic acid solution by Lindner (*Sitzungsber. K. Akad. Wiss. Wien*, 1907, **116**, 945), and found to be unimolecular, but the rate of decomposition of the acid alone does not appear to have been determined.

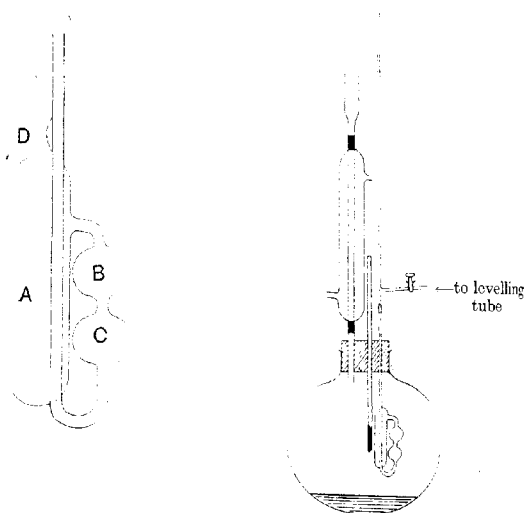
The acid was prepared in the ordinary way from chloroacetic acid, and was twice recrystallised from pure ether. Two preparations melted at  $133.9^{\circ}$  (corr.) and  $134.3^{\circ}$  respectively, the melting point being difficult to determine with great precision owing to incipient decomposition. (Values given in the literature vary from  $131^{\circ}$  to  $134^{\circ}$ .)

The apparatus for measuring the rate of decomposition manometrically is shown in Fig. 1. *A* is a glass bulb of about 20 c.c. capacity, into which small quantities of malonic acid, usually about 20 milligrams, are introduced. *C* is a reservoir containing mercury for the manometer, whilst *B* acts as a trap, preventing mercury from *C* from entering the bulb *A*. When the acid has been introduced into *A* and the mercury into *C*, the apparatus is sealed off at *D*. The decomposition bulb was heated either in a vapour bath or in an electrically heated and controlled oil thermostat. The arrangement of the apparatus when the vapour-bath was used is shown in the right-hand sketch of Fig. 1. The large globe contains a liquid of suitable boiling point (bromobenzene, propylene bromide, tetrachloroethane, xylene, amyl acetate, acetic anhydride, ethylene dibromide, amyl alcohol, and glacial acetic acid were employed). The decomposition bulb is joined by means of pressure tubing to the long manometer tube, which communicates by the tap to a levelling tube containing mercury. The method of taking readings was as follows. When a constant temperature had been attained, the mercury had usually risen to a point not far below the T-piece leading to the levelling tube.



The tap was opened and the pressure increased until the mercury in the decomposition vessel reached a fixed mark between the bulbs *B* and *C*. As decomposition proceeded, the pressure required to bring the contents of *A* and *B* back to constant volume increased and measured the progress of the reaction. When connexion was first made between the manometer and the levelling tube, air bubbles were usually introduced. These were easily removed by pushing a long piece of fine capillary tube down the manometer. The thermometers were compared with a standard thermometer, and the bulb was always placed close to the acid in *A*. Care was

FIG. 1



taken that the condenser runnings did not touch the thermometer or the bulb *A*. For the shorter experiments, this arrangement was very satisfactory, but for longer experiments, owing to barometric changes, the electrically controlled thermostat was preferable. The heating arrangement in this consisted of about a metre of "nichrome" wire with a resistance of 50 ohms wound on a mica frame and immersed directly in the oil-bath. It was connected with the 100-volt main in parallel with the motor driving the stirrer. The regulator was filled with quinoline. Auxiliary heating was provided by a Bunsen burner. The mean temperature remained very constant, but it was impossible to suppress a rapid

periodic fluctuation. As this amounted to about  $\pm 0.3^\circ$  with a two-minute period, and this arrangement was only used with experiments lasting many hours, the regular variations were of no account. The manometric readings were corrected for barometric changes.

At temperatures above the melting point, the amount of drying of the acid does not appear to influence the result, nor were divergences shown by two separate preparations of malonic acid.

The following table gives the results obtained at different temperatures for the fused acid above its melting point and for the supercooled acid. It was found possible to keep it supercooled at  $125^\circ$ .

TABLE I.

$t$  = time in minutes;  $p$  = pressure in mm.;  $p_\infty$  = final pressure;

$$k = \frac{1}{t} \log_{10} \frac{p_\infty}{(p_\infty - p)},$$

Temperature $153.6^\circ$ .			Temperature $136.4^\circ$ .			Temperature $129.4^\circ$ . Liquid supercooled.		
$t$ .	$p$ .	$k$ .	$t$ .	$p$ .	$k$ .	$t$ .	$p$ .	$k$ .
6.5	57	0.0265	10	37.0	0.00568	20	70	0.00263
10.0	85	0.0290	15	53.0	0.00559	35	117	0.00262
14.5	108	0.0288	20	67.0	0.00545	52	167	0.00265
29.0	152	0.0304	27	87.0	0.00547	68	216	0.00276
100.0	175		35	108.0	0.00549	82	251	0.00278
Final	175		45	131.0	0.00549	100	292	0.00280
Mean value of $k=0.0287$			56	155.0	0.00558	120	332	0.00281
			64	171.0	0.00566	135	361	0.00285
			100	223.5	0.00585	166	418	0.00298
			Final	302.0		195	462	0.00305
			Mean value of $k=0.00558$			Final	615	
								Mean 0.00279

Other values obtained were:

Temperature .....	$153.2^\circ$	$143.5^\circ$	$142.3^\circ$	$134.2^\circ$	$133.6^\circ$	$125.9^\circ$
Mean value of $k$ .....	0.0279	0.0099	0.00947	0.00456	0.00397	0.00204*

\* Liquid supercooled.

In calculating  $k$ , the variation in the association of the acetic acid vapour was not taken into account.

In Fig. 2, the decimal logarithm of  $K$  ( $=k \times 10^3$ ) is plotted against the temperature. There is no regular deviation from a straight line. By the method of least squares, the following expression is deduced:

$$\log_{10} K = 0.04157(T - 100) - 0.7778 \quad (1)$$

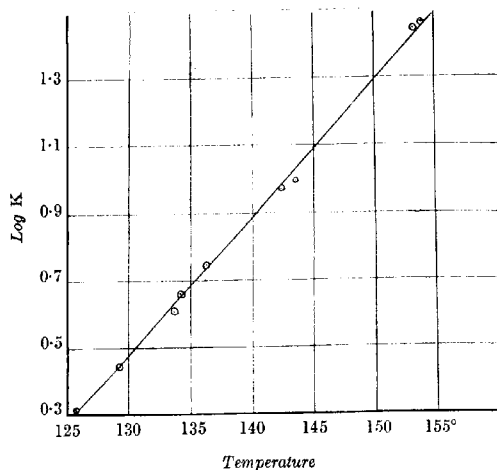
where  $T$  = temperature.

The following table shows the degree of validity of the expression:

Temperature.	$K$ (calculated).	$K$ (found).
153.6°	23.2	28.7
153.2	27.2	27.9
143.5	10.7	9.9
142.3	9.56	9.47
136.4	5.44	5.58
134.2	4.41	4.56
133.6	4.16	3.97
129.4	2.78	2.79
125.9	1.99	2.04

It may therefore be employed to calculate  $K$  for the supercooled liquid at points not far outside the range of temperature actually

FIG. 2.



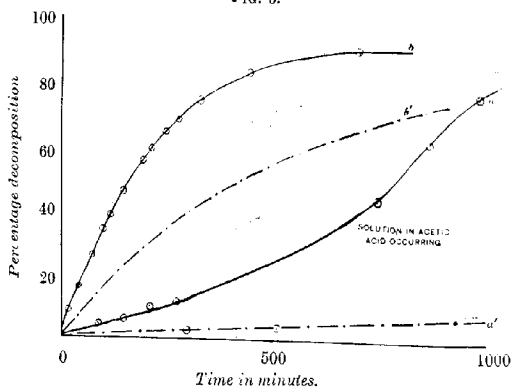
observed, so that comparison may be made between the behaviour of the supercooled liquid and that of the solid.

The solid is much less reactive than the supercooled liquid, the value of  $k$  being of quite a different order of magnitude. It must be stated at the outset, however, that  $k$  for the solid is a much less well-defined constant and difficult to measure accurately, since it appears to be greatly influenced by traces of moisture and mode of preparation of the sample, which conditions are quite unimportant in the case of the liquid.

It was hoped that by the use of small quantities and by work-

ing at temperatures above the boiling point of acetic acid, disturbances due to the condensation of acetic acid would be avoided. This was only partly realised. It was possible to measure the rate of decomposition of the solid acid over a considerable range, but not over the whole range, since at a certain point, depending on the temperature and the relation between the weight of malonic acid and the volume of the bulb, acetic acid began to condense and dissolve the solid. The very slow rate of reaction then increased, and the nature of the curve changed. Fig. 3 illustrates this point. The curves *a* and *a'* show the rate of decomposition of the solid at  $125.9^{\circ}$  and  $116.5^{\circ}$  respectively. Curve *b* shows the rate of decomposition of the supercooled liquid at  $125.9^{\circ}$  as actually

FIG. 3.



*a.* Solid at  $125.9^{\circ}$       *b.* Supercooled liquid at  $125.9^{\circ}$  (experimental curve).  
*a'.* „  $116.5^{\circ}$       *b'.* „ „  $116.5^{\circ}$  (calculated).

measured, whilst curve *b'* shows that of the supercooled liquid at  $116.5^{\circ}$ , calculated from the value of *k* given by equation (1). The rapid increase in rate of reaction when the acetic acid begins to condense and dissolve the malonic acid is observable in curve *a*. An exactly similar phenomenon was later observed in the case of *a'*, but the scale of the diagram does not allow it to be shown. It will be seen, however, from the figures given below.

Values of *k* for the solid deduced from experiments of this sort would not be trustworthy. The following method was therefore adopted. Weighed quantities of malonic acid—from five to ten times the amounts used in the above experiments—were heated in vessels of accurately known volume. The initial rate of decom-

Temperature 125.9°.

(a) Solid.		(b) Supercooled liquid.	
<i>t.</i>	<i>p</i> expressed as percentage of final pressure.	<i>t.</i>	<i>p</i> expressed as percentage of final pressure.
90	4.7	22	9.1
150	6.9	26	11.4
210	10.8	44	17.9
270	12.6	60	23.3
750	48.7	75	28.2
870	68.7	103	37.3
990	84.8	121	42.0
1110	93.4	149	50.3
1230	97.9	170	55.4
1350	99.5	195	60.9
2500	100.0	216	65.3
		250	71.0
		279	75.4
		327	81.8
		445	92.0
		511	97.1
		705	100.0
		1365	100.0

Temperature 116.5°.

(a) Solid.		(b) Liquid supercooled. Calculated from value $k = 0.00081$ given by equation (1).	
<i>t.</i>	<i>p</i> expressed as percentage of final pressure.	<i>t.</i>	<i>p.</i>
240	1.2	119	20
300	2.4	274	40
511	4.05	491	60
1090	9.5	863	80
1210	10.7		
1390	12.8		
1575	15.0		
1725	17.0	Solution in the acetic acid accompanied by a rapid increase in rate.	
1948	19.55		
2558	29.4		
2808	34.7		
3030	40.3		
3200	45.5		
3372	53.2		
4001	89.3		
4291	96.1		
4686	99.0		
5500	100.0		

position, conveniently expressed in c.c. of gas at N.T.P. per gram of malonic acid, could thus be measured without any reference to the later stages of the reaction. Little trouble was caused by acetic acid in these early stages. Slight acceleration

was still sometimes observed, due, presumably, to the retention of acetic acid by the solid. It was in all cases slight and easily eliminated by expressing the rate as a function of the form  $ax+b$  (where  $x$ =the amount of decomposition).  $a$  being quite small, approaching zero,  $b$ , the true initial rate, was obtained without appreciable error. In order to arrive at  $k$  from the initial rates thus measured without making any assumptions as to the state of association of acetic acid vapour, etc., an exactly similar experiment was carried out with the liquid acid, for which  $k$  was known. In this way, the factor was directly obtained for converting "initial rates" into velocity constants.

Temperature 132.2°. Molten acid,  $k=0.00364$ .

Time in minutes.	C.c. reduced to N.T.P. (assuming gas laws); calcu- lated on 1 gram of malonic acid.
2.0	4.5
7.0	14.0
12.0	23.8
19.5	38.1

that is, initial rate = 1.92 c.c. per gram per minute.

An initial rate of 1.92 c.c. per gram per minute thus corresponds with  $k=0.00364$ .

The following rates were determined with the carefully dried solid from the same preparation, and although the actual values cannot be regarded as indicating more than the order, for the reasons given above, they are of some interest.

TABLE II.

Temperature 126.3°.		Temperature 125.5°.	
Minutes.	C.c. per gram of malonic acid.	$t$ .	$x$ .
30	4.9	90	12.0
90	12.4	180	20.8
120	16.4	300	35.7
150	19.7	450	54.7
210	27.3		
270	38.4		
351	57.2		
$\left(\frac{dx}{dt}\right)_0 = 0.134$		$\left(\frac{dx}{dt}\right)_0 = 0.117$	
whence $k = \frac{0.134 \times 0.00364}{1.92}$		whence $k = \frac{0.117 \times 0.00364}{1.92}$	
$= 0.00025$		$= 0.00022$	

TABLE II. (*continued*).

Temperature 121.2°.		Temperature 117.3°.	
C.c. per grain of malonic acid.			
Minutes.			
<i>t.</i>	<i>x.</i>	<i>t.</i>	<i>x.</i>
60	1.8	60	1.9
126	3.5	120	2.8
186	5.4	180	4.1
253	7.4	265	6.5
604	20.6	373	9.7
		465	12.8
$\left(\frac{dx}{dt}\right)_0 = 0.026$		$\left(\frac{dx}{dt}\right)_0 = 0.0215$	
whence $k = \frac{0.026 \times 0.00364}{1.92}$		whence $k = \frac{0.0215 \times 0.00364}{1.92}$	
$= 0.000049$		$= 0.000041$	

## Temperature 110.8°.

<i>t.</i>	<i>x.</i>
150	1.04
240	1.76
425	3.39
$\left(\frac{dx}{dt}\right)_0 = 0.0065$	
whence $k = \frac{0.0065 \times 0.00364}{1.92}$	
$= 0.000012$	

Temperature.	<i>k</i> for the solid acid.	<i>k</i> for the super-cooled liquid.	Ratio.
126.3°	0.00025	0.00207	8
125.5	0.00022	0.00192	9
Rejected (121.2	0.000049	0.00127	26)
117.3	0.000041	0.00087	21
110.8	0.000012	0.00047	39

From the increase in the ratio in the last column, as the temperature falls it appears that the temperature-coefficient for the solid is much greater than that for the liquid measured over the same range, so that, as the temperature decreases, the difference between the reactivity in the two states becomes more and more pronounced. One would expect the statistical energy-distribution curve of the solid to approach that of the liquid in the neighbourhood of the melting point. In criticism, it must be remarked that any impurities, such as occluded solvent, would give rise to increasing amounts of liquid phase as the temperature approached the melting point. This would lead to an unduly large temperature-coefficient, since the variation, due solely to increase in temperature, would be superimposed on that due to the increased amount of liquid phase.

In view of the fact that the malonic acid was carefully purified and melted at the correct temperature, it is almost impossible that this would account for more than a small fraction of the increased temperature-coefficient. Otherwise visible amounts of liquid should have been observed at  $125^{\circ}$ , whilst actually no trace was noticed. Nevertheless, the criticism must be borne in mind until further experiments are made.

The discussion of the bearing these results may have on the radiation hypothesis may be left until the study of the infra-red properties is completed.

In conclusion, I have pleasure in thanking Mr. H. B. Hartley and Mr. D. H. Nagel for much help and advice.

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## Organic Chemistry.

**Action of Selenyl Chloride on Unsaturated Compounds.**

ARNO MÜLLER (*Chem. Zeit.*, 1919, **43**, 843).—Preliminary qualitative experiments show that selenyl chloride combines with unsaturated hydrocarbons and ketones to form well-defined, crystalline additive compounds which are somewhat unstable towards light and air, and are readily decomposed by boiling water into selenyl chloride and the corresponding hydrocarbon or ketone. Thionyl chloride also unites with olefinic substances to give small amounts of deeply coloured additive products, but the reaction is generally uncontrollably violent, and the formation of by-products cannot be avoided.

H. W.

**Removal of Aromatic Hydrocarbons from Mineral Oils by means of Trioxymethylene-sulphuric Acid.**

JENŐ TARSZ (*J. pr. Chem.*, 1919, [ii], **99**, 276–280).—Nastkujoff's formolite reaction (*A.*, 1904, i, 801) for aromatic hydrocarbons is also shown by diolefines, such as methyl- and dimethyl-butadienes, which contain conjugated double bonds, owing to their condensation to ring compounds under the influence of sulphuric acid. On the other hand, the reaction is limited in the case of aromatic hydrocarbons to those containing a hydrogen atom in the nucleus, since hexamethyl- and hexaethyl-benzenes do not answer to it. Aromatic hydrocarbons are usually completely removed from mineral oils by this method, or by Herr's modification (*A.*, 1910, ii, 904) only after a repetition of the treatment, owing to gradual dilution of the sulphuric acid. The author overcomes this difficulty by the use of trioxymethylene in place of formaldehyde solution or methylal. [See, further, *J. Soc. Chem. Ind.*, 1920, February.]

J. K.

**Action of Fluorine on Organic Compounds.**

BURR HUMISTON (*J. Physical Chem.*, 1919, **23**, 572–577).—The action of fluorine on organic compounds is usually violent, leading to decomposition. Saturated hydrocarbons are ignited with incandescence and formation of free carbon, carbon fluorides, and hydrogen fluoride. "Filtchar" charcoal is attacked at the ordinary temperature, a gas, non-liquefiable at  $-80^{\circ}$ , being the chief product, accompanied by carbon tetrafluoride and tetrafluoroethylene (compare Moissan, *A.*, 1890, 55). Selenium also yields as chief product a gas, which escapes liquefaction at  $-80^{\circ}$  (compare Prideaux, *T.*, 1906, **84**, 316). Acetone is ignited by pure fluorine, whilst, in presence of an indifferent gas, charring takes place and some tetrafluoroethylene is produced. An indefinite product containing some carbonyl chloride is obtained from chloroform. Carbonyl chloride appears to be unattacked at  $6^{\circ}$ , but apparently some carbonyl fluoride is

produced at 200°. No evidence could be obtained of a reaction with carbon monoxide. Carbon tetrachloride is only slightly attacked at the ordinary temperature, but tetrachloroethylene gradually blackens even at 0°, hexachloroethane being among the products. J. K.

**Tetrachlorodinitroethane.** W. L. ARGO, E. M. JAMES, and J. L. DONNELLY (*J. Physical Chem.*, 1919, **23**, 578—585. Compare Biltz, A., 1902, i, 417).—Tetrachlorodinitroethane is very soluble in liquid nitrogen tetroxide, and has pronounced toxic and lachrymatory properties. The optimum temperature for its production from dry liquid nitrogen tetroxide and tetrachloroethylene is 80°. [See, further, *J. Soc. Chem. Ind.*, 1920, 82A.] J. K.

**Preparation of Ethyl Alcohol.** ELEKTRIZITÄTSWERK LONZA (Brit. Pat. 134521).—In the catalytic reduction of acetaldehyde to ethyl alcohol by means of hydrogen, the excess being returned to the operation by a circulating device (Brit. Pat. 120163), the production of ethyl ether as a by-product, and the gradual poisoning of the catalyst by the decomposition products of acetaldehyde, are avoided by circulating with the hydrogen an amount of oxygen not exceeding 0.3%. The temperature of the reaction chamber is maintained between 90° and 170° by cooling, or preferably by using the hydrogen in such excess that it absorbs and removes the superfluous heat of the reaction. Whereas without the use of oxygen the yield of alcohol fell after thirty hours nearly to zero, an average yield of 95% of the alcohol theoretically possible was obtained in a run extending over two hundred and eleven hours, in which 0.15% of oxygen was used. This beneficial effect of the oxygen cannot be attributed to the complete oxidation of carbon monoxide, methane, etc., to the presence of which the injurious effect on the catalyst is ascribed. G. F. M.

**Melissyl Alcohol and Melissic Acid.** A. HEIDUSCHKA and M. GAREIS (*J. pr. Chem.*, 1919, [ii], **99**, 293—311).—The formula for melissyl alcohol has been considered by some workers to be  $C_{30}H_{61}\cdot OH$ , by others  $C_{31}H_{63}\cdot OH$ . The authors have therefore prepared a series of derivatives of melissyl alcohol from carnauba wax and from beeswax, and confirmed the view of Schwalb (A., 1885, 962) that the alcohols from these sources differ. The former has the formula  $C_{30}H_{61}\cdot OH$ , whilst that of the latter is  $C_{31}H_{63}\cdot OH$ . The melting points of their respective derivatives were as follows (those of carnauba melissyl alcohol being quoted first): *acetates*, 74° and 70°; *benzoates*, 69.5° and 66°; *phthalates*, 82° and 81.5°; *monochloroacetates*, 79.5° and 74°; *phenylurethanes*, 98° and 96°; *chlorides*, 67° and 65°; *bromides*, 68° and 67°; *iodides*, 69.5° and 68°. Carnauba melissyl alcohol on oxidation by Iell's process (A., 1884, 1433) gave a melissic acid,  $C_{30}H_{60}O_2$ , m. p. 90° (lead salt, m. p. 118°), whilst the acid,  $C_{31}H_{62}O_2$ , from beeswax had m. p. 88.5° (lead salt, m. p. 115°). The latter acid was also obtained by

hydrolysis of carnauba melissyl cyanide, which in an impure condition melted at 75°.

Stürcke's observation (A., 1884, 1280) that carnauba melissyl alcohol is accompanied by an alcohol,  $C_{27}H_{56}O$ , m. p. 76°, was also confirmed.

J. K.

**Phytochemical Reduction of Ketones. Biochemical Preparation of Optically Active Secondary Alcohols.**

C. NEUBERG and F. F. NORD (*Ber.*, 1919, 52, [B], 2237—2248).—The authors find that the phytochemical reduction of the ketonic group is frequently possible both with aromatic and aliphatic ketones, and leads to the production of the corresponding secondary alcohols. Hydrogenation is more difficult than with the aldehydes, since it proceeds more slowly and less completely, and also requires more energetic conditions. The biological nature of the process is shown by the fact that the secondary alcohols are optically active, an asymmetric carbon atom being developed during the process. They have been isolated in the chemically pure condition, but the yields are poor (about 10%) and a considerable portion of the original material remains unattacked, and is subsequently removed by treatment with sodium hydrogen sulphite or hydrazine bases. They are not optically pure. Acetaldehyde is invariably also formed, the oxidative production of which is probably the complementary process of the hydrogenation of the ketone.

The mixtures were generally made from conductivity water (2 litres) at 35—40°, sucrose (200 grams), yeast (200 grams) and the ketone (10—15 grams), and fermentation was allowed to proceed for three to six days, frequently followed by a second addition of sucrose and yeast and renewed fermentation. In this manner methyl ethyl ketone yielded *d*-methylethylcarbinol, b. p. 99—100°,  $[\alpha]_D^{20} + 3.34^\circ$ , methyl *n*-propyl ketone gave *d*-methyl *n*-propylcarbinol, b. p. 117—119°,  $[\alpha]_D^{20} + 6.3^\circ$ ,  $D^{20}_D 0.810$ , methyl *n*-hexyl ketone yielded *d*-methylhexylcarbinol, b. p. 177—179°,  $[\alpha]_D^{20} + 2.85^\circ$ , whilst *d*-methylnonylcarbinol, b. p. 228—229°,  $[\alpha]_D^{20} + 2.95^\circ$ , and *l*-phenylmethylcarbinol, b. p. 202—204°,  $[\alpha]_D^{20} - 8.01^\circ$ , were prepared from methyl nonyl ketone and acetophenone respectively.

H. W.

**Phytochemical Reduction of Diketones.** C. NEUBERG and F. F. NORD (*Ber.*, 1919, 52, [B], 2248—2254. Compare preceding abstract).—The authors find that diacetyl can be readily hydrogenated by biochemical methods, and that *l*-β-γ-butylene glycol is produced in yield which is regarded as satisfactory when the difficulties of isolation are taken into consideration; the optical activity of the product is the more remarkable, since Harden and Walpole have found that the action of bacteria on a series of carbohydrates leads to a mixture of the racemic and meso-forms of the glycol. Under similar circumstances, benzil yields benzoin, which in the main is optically inactive, but which contains small amounts of *l*-benzoin. Attempts to reduce benzil or benzoin to the corresponding glycol were unsuccessful.

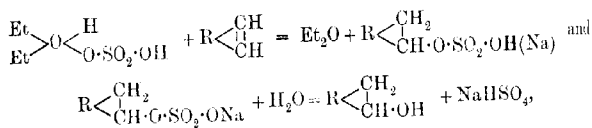
H. W.

### Addition Catalysis by means of Diethyloxonium Salts,

Et  $\begin{smallmatrix} >O < H \\ Et & R \end{smallmatrix}$  OSSIAN ASCHAN (*Medd. K. Vetenskapsakad. Nobel. Inst.*, 1919, 5, No. 8, 1—32).—Reference is first made to the use of ethereal solutions of hydrogen chloride in the synthesis of hydrochlorides in the terpene series (compare A., 1916, i, 51), and it is pointed out that without the use of ethyl ether as catalyst tertiary pinene hydrochloride (*Öfvers. Finska Vet.-Soc. förh.*, 1914—1915, 57, [1], No. 1) could not have been prepared. The results thus obtained with the ether-additive product of hydrogen chloride led the author to investigate the addition of water to unsaturated compounds by means of a mixture of absolute ether and sulphuric acid monohydrate. When this mixture is made there is a large development of heat, and when the two components are in equivalent quantities the resulting mixture is much more viscous than the sulphuric acid. It is concluded that diethyloxonium sulphate,  $\text{OHEt}_2\text{O}\cdot\text{SO}_2\cdot\text{OH}$ , is formed, although neither it nor a salt could be isolated.

The method of experiment was generally to dissolve the sulphuric acid monohydrate in the molecular quantity of ethyl ether, or, if necessary, in an excess of ether, well cooling meanwhile, and then add the unsaturated compound in small portions at a time, again well cooling. In some experiments a further quantity of water was added to the sulphuric acid monohydrate. After keeping for some time the resulting mixture was poured into an excess of sodium carbonate solution and the products isolated by steam distillation and subsequent fractionation.

The normal reaction would be represented by the equations:



the alcohol being produced, but in some cases, possibly when the reaction mixture is poured into the sodium carbonate solution, fission of water takes place with reproduction of the original compound or an isomeride; di- and poly-terpenes may also be produced.

Camphene hydrate and santenol, which are among the lesser sensitive alcohols, are the main products of reaction from camphene and santene, but some of the original substances are re-formed, either as such or as diterpenes. The more sensitive alcohols, which should result from such substances as pinene, nopinene, etc., are not produced, either the original compound being re-formed or else a polymerisation product obtained. In the case of  $\beta$ -methyl- $\Delta^3$ -butylene, the dipolymeride, diamylene, is readily obtained in an almost pure condition, together with smaller quantities of tertiary isoamyl alcohol.

Absolute ethyl ether and colourless concentrated nitric acid, when mixed in small quantities, give a mixture, which is stable for a

short time. Diethylxonium nitrate may be present in such a mixture. T. S. P.

### Kephalin. VII. The Glycerophosphoric Acid of Kephalin.

P. A. LEVENE and IDA P. ROLF (*J. Biol. Chem.*, 1919, **40**, 1—16).

The generally accepted formula of kephalin presumes the existence of glycerophosphoric acid in the molecule, but the experimental evidence produced so far in support of this supposition is not convincing. The presence of glycerol in kephalin has been satisfactorily demonstrated (Foster, A., 1915, ii, 493). Theoretically, there are only two alternative ways in which glycerol may be attached to phosphoric acid, either directly with the formation of glycerophosphoric acid, or indirectly with the glycerol attached to the aminoethyl alcohol. If the latter condition existed, the amino-group of the kephalin molecule would not be free. Since it has been experimentally shown that the amino-group is free, it follows that the presence of glycerophosphoric acid in kephalin could have been accepted before the substance was actually isolated.

The glycerophosphoric acid isolated from the hydrolysis of kephalin possesses an optical rotation of the same magnitude as the acid from lecithin, namely,  $[\alpha]_D^{20} = -0.69^\circ$ . This work establishes the fact that glycerophosphoric acid exists in kephalin, and that the acid is identical with that present in lecithin. The crude barium glycerophosphate from kephalin shows dextrorotation, which may account for the statement made by Fränkel and Dimitz (A., 1909, i, 870) that the glycerophosphoric acids present in lecithin and kephalin are optical isomerides. The authors have now shown, however, that on purification the dextrorotation is lost. It is probably due to admixture of the barium glycerophosphate with a dextrorotatory product of intermediary hydrolysis. The authors are unable to confirm the observations of Willstätter and Lüdecke, who stated that the optical rotation of the glycerophosphoric acid from lecithin differs according to the mode of preparation. The maximum rotation for the glycerophosphoric acid from lecithin is found to be  $[\alpha]_D^{20} = -0.74^\circ$ , a value lower than that recorded by Willstätter and Lüdecke (A., 1904, i, 1067).

J. C. D.

### The History of Zeise's Mercaptan and its Name (1833).

PAUL DIERGART (*J. pr. Chem.*, 1919, [iii], **99**, 281—292).—Historical.

J. K.

### Preparation of Ethylene Ethylidene Disulphide. OSKAR

MATTEI (D.R.-P. 313650; from *Chem. Zentr.*, 1919, iv, 617—618).

When the amorphous ethylene sulphides,  $(C_2H_4S)_n$ , m. p.  $145^\circ$  and  $176^\circ$  respectively (prepared by the action of ethylene chloride or bromide on aqueous or alcoholic solutions of alkali sulphides), are heated almost to dull redness in the absence of air, the main portion distils as *ethylene ethylidene sulphide*, leaving only an unimportant charcoal-like residue. Decomposition occurs more smoothly when a solid substance, such as a metallic sulphide, is

added to the ethylene sulphide and when a slow current of hydrogen sulphide is sent through the apparatus. After being frozen out, the crude material is purified by passage through a tube loosely packed with fragments of porous pot and heated at about  $300^{\circ}$ . The vapours are collected in a well-cooled receiver. Ethylene ethylidene disulphide, after being shaken with aqueous alkali, is obtained as an almost colourless liquid, b. p.  $172-173^{\circ}$ , which is a good solvent for organic substances and may serve as a basis for pharmaceutical preparations. H. W.

**Volatility with Steam of Lower Fatty Acids in Dilute Aqueous Solution.** EDGAR J. WITZEMANN (*J. Amer. Chem. Soc.*, 1919, **41**, 1946—1951).

—The volatility in steam of formic acid, acetic acid, propionic acid, and butyric acid has been examined by distilling equivalent solutions (about 1%) and analysing the distillates. The volatility is shown to increase with increasing molecular weight. Thus the first fraction (20 c.c.) to distil over contains 6.92% of the acetic acid, 3.94% of the formic acid, 12.4% of the propionic acid, and 19.5% of the butyric acid, whilst the residue (15 c.c.), after distillation of 180 c.c., contains 36.8% of the formic acid, 18.6% of the acetic acid, 5.7% of the propionic acid, and 1.4% of the butyric acid. This behaviour is explained as due to the hydration of the acids to form stable complexes, which lower the vapour pressure of the solution. The addition of potassium chloride or magnesium chloride to solutions of formic or acetic acid increases the volatility of the acids. The increase in volatility depends on the concentration of the salt, and also on its nature. Thus 0.5*N*-potassium chloride has about the same effect as 0.2*N*-magnesium chloride. Using a series of salts in 0.25*M* quantities in formic acid solution, the volatility in steam is increased in every case, the order being an increasing volatility with decreasing electro-affinity of the metallic ion of the salt for the chlorides of potassium, sodium, barium, strontium, calcium, magnesium, and aluminium. The chlorides of iron, manganese, and copper are irregular in their action. J. F. S.

**The Chlorination of Methyl Formate and Chloroformate.**

V. GRIGNARD, G. RIVAT, and ED. URBAIN (*Compt. rend.*, 1919, **169**, 1074—1077. Compare Kling, Florentin, Lassieur, and Schmutz, this vol., i. 8).—Light exerts a marked influence on the chlorination of methyl chloroformate. In diffused light it is only the chloromethyl ester which is formed, bright sunlight being necessary for the formation of the di- or tri-chloromethyl ester. In ultra-violet light the trichloro-ester is easily obtained. The effect of temperature is such that up to  $110-112^{\circ}$  the chlorination proceeds smoothly, but at  $113-114^{\circ}$  it slackens very noticeably and at  $117^{\circ}$  decomposition begins to take place with the formation of carbonyl chloride.

Catalysts, such as ferric chloride, antimony chloride, etc., are beneficial at first in the formation of the dichloromethyl ester, but

when a certain concentration is reached decomposition commences, and may continue indefinitely, as some of the perchloride becomes dissolved in the liquid and continues its action.

W. G.

**The Chloro-derivatives of Methyl Formate and Methyl Carbonate.** V. GRIGNARD, G. RIVAT, and ED. URBAIN (*Compt. rend.*, 1919, **169**, 1143—1147. Compare this vol., i, 8, and preceding abstract).—A study of the properties of the chloromethyl chloroformates and of chloro-derivatives of methyl carbonate.

Chloromethyl chloroformate,  $\text{ClCO}_2\cdot\text{CH}_2\text{Cl}$ , is a lachrymatory liquid and has b. p.  $106.5^\circ$ ,  $D^{14}_D$  1.456,  $n^{20}_D$  1.42837. Dichloromethyl chloroformate is a lachrymatory liquid, b. p.  $46^\circ/62$  mm. and  $111^\circ$ ,  $D^{17}_D$  1.558,  $n^{20}_D$  1.44322. Trichloromethyl chloroformate is less lachrymatory but more suffocating than the two preceding esters, and has b. p.  $125\text{--}126^\circ/748$  mm.,  $D^{15}_D$  1.644,  $n^{20}_D$  1.45664.

By moderate chlorination of methyl chloroformate in diffused sunlight trichloromethyl carbonate, b. p.  $138^\circ$ ,  $D^{25}_D$  1.297,  $n^{20}_D$  1.41160, is obtained as one of the products. Dichloromethyl methyl carbonate has b. p.  $48\text{--}49^\circ/18$  mm.,  $D^{17}_D$  1.412,  $n^{20}_D$  1.42852. Chloromethyl dichloromethyl carbonate, one of the products of the more intense chlorination of methyl chloroformate, has b. p.  $96^\circ/45$  mm. and  $177\text{--}179^\circ$ ,  $D^{18}_D$  1.553,  $n^{20}_D$  1.45414. Methyl trichloromethyl carbonate has b. p.  $59.5\text{--}60^\circ/16$  mm. and  $161\text{--}163^\circ$ ,  $D^{17}_D$  1.525,  $n^{20}_D$  1.44964. *s*-Tetrachloromethyl carbonate, b. p.  $83^\circ/19$  mm. or  $93\text{--}94^\circ/20$  mm.,  $D^{18}_D$  1.630,  $n^{20}_D$  1.46306, is one of the products of the chlorination of methyl chloroformate in a leaden vessel. By carrying the chlorination still further, hexachloromethyl carbonate, m. p.  $79^\circ$ , is obtained.

W. G.

**Properties of the Chloromethyl Chloroformates.** ANDRÉ KLING, D. FLORENTIN, A. LASSIEUR, and E. SCHMUTZ (*Compt. rend.*, 1919, **169**, 1166—1168).—A study of the physical and chemical properties of the mono-, di-, and tri-chloromethyl chloroformates.

The purest specimen of chloromethyl chloroformate contained 8.6% of the dichloromethyl ester. It had b. p.  $52.5\text{--}53^\circ/100$  mm. and  $106.5\text{--}107^\circ/700$  mm.,  $D^{15}_D$  1.465. It is both lachrymatory and suffocating. It is quantitatively decomposed by water according to the equation  $\text{Cl}\cdot\text{CO}_2\cdot\text{CH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{H}\cdot\text{CHO} + \text{CO}_2 + 2\text{HCl}$ . With alcohols it gives the corresponding mixed chloromethyl carbonates, and with sodium phenoxide it gives *phenyl chloromethyl carbonate*, b. p.  $122\text{--}124^\circ/13$  mm.,  $D^{23}_D$  1.255. Anhydrous aluminium or ferric chloride decomposes chloromethyl chloroformate at  $70^\circ$ , giving carbonyl chloride.

Dichloromethyl chloroformate has b. p.  $54\text{--}55^\circ/100$  mm. and  $110\text{--}111^\circ/700$  mm.,  $D^{15}_D$  1.560. On hydrolysis it yields carbon monoxide, carbon dioxide, and hydrogen chloride. With alcohols it gives the mixed dichloromethyl carbonates, and with sodium phenoxide *phenyl dichloromethyl carbonate*, m. p.  $14.5^\circ$ , b. p.  $124\text{--}125^\circ/14$  mm.,  $D^{15}_D$  1.34.

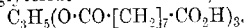


Trichloromethyl chloroformate has b. p.  $49^{\circ}/50$  mm. and  $127^{\circ}/750$  mm.,  $D^{15}_4$  1.653. Its general properties resemble those of carbonyl chloride. On hydrolysis it gives carbon dioxide and hydrogen chloride, and with aniline water it yields *s*-diphenylcarbamide. With alcohols it gives the mixed trichloromethyl carbonates, and with sodium phenoxide yields *phenyl trichloromethyl carbonate*, m. p.  $166^{\circ}$ .

Anhydrous aluminium or ferric chloride decomposes it, giving carbon tetrachloride and carbon dioxide. W. G.

#### Determination of the Position of the Double Linking and its Transposition in some Unsaturated Compounds.

(MILLER.) A. C. NOORDUYN (*Rev. trav. chim.*, 1919, **38**, 317—344).—The method adopted was to convert the unsaturated compound into its ozonide and decompose this by boiling it with water, the resulting aldehydes being, if necessary, oxidised to the acids for purposes of identification. By this method Goldsobel's formula for ricinoleic acid,  $\text{CH}_3[\text{CH}_2]_5\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}:\text{CH}[\text{CH}_2]\cdot\text{CO}_2\text{H}$  (compare A., 1895, 81), has been confirmed. Further evidence in support of this was obtained by the ozonisation of castor oil and subsequent decomposition of the ozonide. One of the products of this action, after oxidation, was the glyceride of azelaic acid,



$D^{15}_4$  1.0377,  $n$  1.4693. Similarly, undecenoic acid was shown to have the formula  $\text{CH}_3\cdot\text{CH}[\text{CH}_2]_8\cdot\text{CO}_2\text{H}$ , and one of the products of decomposition of its ozonide was the semi-aldehyde of sebacic acid, m. p.  $126^{\circ}$ , giving a *semicarbazone*, m. p.  $168^{\circ}$ .

Three unsaturated hydrocarbons, octylene, decylene, and heptadecylene, were prepared by the method of Grosjean (compare A., 1892, 691) by heating the barium salt of the next higher acid with sodium ethoxide, and it was shown by the ozonide method that the products, in every case, were mixtures of isomeric hydrocarbons. Similarly, the  $\beta$ -octylene of Kahlbaum, prepared by the action of zinc chloride on secondary octyl alcohol, was shown to be a mixture of isomerides.

By the fusion of oleic acid with potassium hydroxide there is formed not only acetic and palmitic acids, but a number of higher homologues of acetic acid and lower homologues of palmitic acid. Under similar conditions elaidic acid also gives a mixture of acids.

W. G.

**Ghedda or East Indian Wax. II. Its Acids.** A. LIEP and EUGEN KOVÁCS (*J. pr. Chem.*, 1919, [ii], **99**, 243—255. Compare A., 1912, i, 675).—The residue of potassium salts, after removal from the wax of alcohols and hydrocarbons in the manner previously described, furnished a mixture of acids, of which one was sparingly soluble in ether (see following abstract). From the remainder, after removal by steam of small amounts of formic and butyric acids, margaric acid and a previously unknown hydroxy-

margaric acid were separated by fractional extraction with light petroleum.

*Hydroxymargaric acid*,  $C_{17}H_{34}O_3$ , m. p.  $58^\circ$ , could not be distilled under reduced pressure. It was characterised as a normal acid by conversion into margaric acid through the action of hydriodic acid successively at  $100^\circ$  and at  $200-220^\circ$ . The intermediate iodomargaric acid was only obtained impure in the form of needles, m. p.  $41.5^\circ$ . J. K.

### Ghedda or East Indian Wax. III. Hydrocarbons and Acids. A. LIPP and E. CASIMIR (*J. pr. Chem.*, 1919, [ii], 99, 256-258).

—The wax contains approximately 48% of ceryl alcohol, 7% of hydrocarbons (5% of heptacosane, 2% of hentriacontane, with traces of a hydrocarbon of low melting point), 24–25% of hydroxymargaric acid, m. p.  $55-56^\circ$  (see preceding abstract), 1.5–2% of an isomeric hydroxymargaric acid, m. p.  $71-72^\circ$ , 9–10% of margaric acid, 8–9% of palmitic acid, 2% of "Ghedda" acid, and 1% of cerotic acid with traces of formic, acetic, and butyric acids and tarry matter. Cerotic and ghedda acids are present mainly in the free condition, the others in the form of their ceryl esters.

"Ghedda" acid, to which the formula  $C_{34}H_{68}O_2$  is provisionally ascribed, m. p.  $94.5-95^\circ$ , forms mossy aggregates of white needles. Its sparing solubility in ether and that of its potassium salt in alcohol permit its separation from the other acids present. It differs from melissic acid, but is possibly identical with an acid obtained by Schalfieff (this Journ., 1877, i, 454; compare, however, Nafzger, A., 1884, 1297).

*Hydroxymargaric acid*,  $C_{17}H_{34}O_3$ , m. p.  $71-72^\circ$ , forms needles or leaflets, and was isolated from the last light petroleum extracts of the mixed acids (see preceding abstract). Its calcium salt,  $Ca(C_{17}H_{33}O_2)_2$ , forms small, spherical nodules.

The hydrocarbon previously described (Lipp and Kuhn, A., 1912, i, 675) as  $C_{30}H_{62}$ , m. p.  $70^\circ$ , is now found to have m. p.  $68-68.5^\circ$ , and considered to be hentriacontane,  $C_{31}H_{64}$ , from its resemblance to the hydrocarbon obtained by Krafft from palmitone (A., 1882, 1272) and its identity with that prepared by Popp (*Diss., Tech. Hochschule*, Munich, 1916), by reducing myricyl alcohol, which, on the other hand, he oxidised to melissic acid, at the same time establishing the formula  $C_{31}H_{62}O_2$  for this acid (but see Heiduschka and Gareis, this vol., i, 134). Also the hydrocarbon,  $C_{26}H_{54}$ , m. p.  $58^\circ$ , is now found to have m. p.  $59.5^\circ$ , and considered to be heptacosane,  $C_{27}H_{56}$ , from its similarity to the hydrocarbon obtained from myristone by Krafft (*loc. cit.*). J. K.

### Crystallographic Investigation of the Dichlorosuccinic

Acids. G. AMISOFF (*Arkiv Kem. Min. Geol.*, 1917-18, 7, No. 9, 1-11).—The optically active dichlorosuccinic acids have m. p.  $166-167^\circ$  and  $D^{25}_D$  1.820. They are monoclinic-sphenoidal [ $a:b:c=2.3351:1:2.3754$ , and  $\beta=101^\circ30'$ ]. Twinning takes place along the plane  $c\{001\}$ , cleavage parallel with  $x\{101\}$ , and optical

extinction parallel to the edges  $[(100):(001)]$  and  $[(001):(011)]$ . The plane of the optical axis is parallel with  $b\{010\}$ .

The racemic acid has m. p.  $174-175^\circ$  and  $D^{25}_D 1.844$ . The crystals are monoclinic-prismatic,  $[a:b:c=0.5846:1:0.5994]$  and  $\beta=100^\circ 46'$ . Cleavage takes place parallel to the axes  $x\{101\}$  and  $b\{010\}$ , and optical extinction parallel with the edges  $[(100):(001)]$  and  $[(001):(010)]$ . The optical axis is parallel with  $b\{010\}$ . It is not certain from the results whether the racemic acid is a true racemate.

*meso*-Dichlorosuccinic acid has m. p.  $217-218^\circ$ . The crystals are monoclinic and needle-shaped, but they were not well enough developed to determine the crystallographic constants. T. S. P.

**Apparatus for the Electrolytic Decomposition of Organic Acids at Low Temperature and with Small Volumes of Liquid. Electrolytic Decomposition of the Alkali Salts of Citraconic Acid.** F. HENRICH and WILHELM SCHENK (*Ber.*, 1919, 52, [B], 2120—2125).—The apparatus consists of a small flask, the bottom of which has been removed and the neck of which is provided with a cork holding a small inverted tube. The latter serves the two-fold function of diminishing the size of the apparatus to the required extent and of allowing efficient cooling by the introduction of a stream of cold water into the tube. As anode, a stout platinum wire or, preferably, a platinum gauze, is placed in close proximity to the tube. The cathode consists of a piece of nickel gauze. The apparatus is conveniently kept at a temperature of  $25-40^\circ$ . A gas-holder of the type previously recommended by Henrich (*A.*, 1909, ii, 66) is used for collection of the anode gases, and arrangements are also described which permit the analysis of these gases at any desired moment.

Electrolysis of concentrated, faintly alkaline solutions of potassium citraconate yields a mixture of oxygen, carbon dioxide, and allylene at the anode, the proportion of the latter increasing with increasing strength of current. Its production is also favoured by high concentration and low temperature, and is found to depend on the particular alkali salt used; the yields increase from lithium through sodium and potassium to rubidium, and then decline to caesium. The authors consider that this behaviour supports the conception of Fichter and Krummenacher (*A.*, 1918, i, 369) that electrolytic decomposition of organic acids is an oxidation process rather than the purely ionic hypothesis of Crum-Brown and Walker. H. W.

**Electrolytic Decomposition of Glutaconic Acid.** F. HENRICH and ADOLF HERZOG (*Ber.*, 1919, 52, [B], 2126—2130).—The electrolytic decomposition of alkaline solutions of potassium glutaconate in the apparatus described in the preceding abstract leads to the formation of acetylene, acetaldehyde, carbon monoxide, and carbon dioxide at the anode, these appearing to be the sole products of the action; the mechanism of the change has not been

fully elucidated, but the results appear to support the oxidation theory of electrolytic decomposition advanced by Fichter and Krummenacher (A., 1918, i, 369).

H. W.

**Glutaconic Acid. III. Condensation of Sodioformyl-acetic Ester with Cyanoacetic Ester.** P. E. VERKADE (*Vers. Akad. Wetensch. Amsterdam*, 1919, 27, 1130—1139).—The product of reaction of these two substances is not ethyl  $\alpha$ -cyano-glutaconate, as stated by other workers, but probably ethyl  $\omega\omega'$ -dicyano-1:3-dimethylcyclobutane- $\omega:\omega':2:4$ -tetracarboxylate.

CHEMICAL ABSTRACTS.

**Preparation of Gluconic Acid.** A. HERZFELD and G. LENART (*Zeitsch. Ver. deut. Zuckerind.*, 1919, 122—128).—Kiliani and Kleemann's method (A., 1884, 993) has been modified in the following manner, so that the use of lead compounds for the elimination of the hydrobromic acid is obviated, the object in view being the elaboration of a technical process for the preparation of a substitute for vegetable acids. One part of dextrose (from starch), dissolved in 5 parts of water, is shaken in a closed vessel with 1 part of bromine until the disappearance of the latter. Oxidation is generally complete after twenty-four hours, at the end of which time the excess of bromine is distilled off in a vacuum, the temperature of the water-bath being about 50°. Heating is continued until the liquid commences to be coloured, when it is diluted with about 350 times its volume of water, and the hydrobromic acid neutralised by sodium carbonate. An excess of calcium carbonate is added gradually at a temperature of 90° (during which operation any lactone formed during distillation is transformed), and after two or three days the calcium salt separates out, and is recrystallised. By working up the mother liquors an almost quantitative yield may be obtained. If invert sugar is used in place of dextrose, the unchanged levulose may be either precipitated as its insoluble calcium salt or converted into levulic acid by boiling with dilute mineral acid.

J. P. O.

**The Hydrates of Heptaldehyde.** (Mlle.) A. C. NOORDUYN (*Rec. trav. chim.*, 1919, 38, 345—350).—An examination of the system heptaldehyde-water shows the existence of a monohydrate and a dihydrate. No evidence of the existence of the hemihydrate described by Bussy (*Annalen*, 1846, 60, 247) could be obtained.

W. G.

**The Stabilisation of Acetaldehyde. IV. Compounds Acting as Stabilisers against the Formation of Disacryl.** CHARLES MOUREU, CHARLES DUFRAISSE, and PAUL ROBIN (*Compt. rend.*, 1919, 169, 1068—1072. Compare A., 1919, i, 574; this vol., i, 10).—A study of the products present in the various fractions obtained by the fractional distillation of acetaldehyde prepared by the dehydration of glycerol with potassium hydrogen sulphate shows that benzoic acid exerts a marked but variable stabilising action.

Phenol, found in some of the fractions, is also a stabilising agent, but its activity is relatively feeble. W. G.

**The Stabilisation of Acraldehyde. V. Stabilising Action of Substances with a Phenolic Group.** CHARLES MOUREU, CHARLES DUFRAISSE, PAUL ROBIN, and JEAN POUGNET (*Compt. rend.*, 1920, **170**, 26-31. Compare preceding abstract).—It has previously been shown that both phenol and benzoic acid exert a marked stabilising action against the formation of disacryl from acraldehyde. The study has now been extended to other phenols and certain hydroxy-acids.

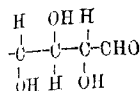
Of the monohydroxyphenols examined,  $\alpha$ -naphthol shows the strongest stabilising action, and the presence of several hydroxy-groups attached to ring carbon atoms causes a notable increase in the stabilising power, except when two hydroxy-groups are in the meta-position to one another. The action of the various hydroxy-benzoic acids is intermediate between that of the phenol and that of benzoic acid itself. Unlike the phenols, their methyl ethers or their acetyl derivatives show little or no stabilising action. Similarly, the alcohols and the polyhydric alcohols do not exercise any stabilising action. Not only do the polyphenols inhibit the formation of insoluble resin (disacryl) from acraldehyde, but they also exercise a similar inhibiting action against the formation of soluble resin, even when the phenol is only present to the extent of 1 in 4000. W. G.

**Oxidation of Mannitol by Nitrous Fumes.** E. VOTOČEK and C. KRAUZ (*Zeitsch. Zuckerind. Böhm.*, 1919, **43**, 577—580).—In the hope of finding a reagent which will effect the oxidation of polyhydric alcohols to either aldehydic or ketonic substances exclusively, the authors have investigated the action of nitrous fumes on an aqueous solution of mannitol; oxidation occurs slowly (but can be accelerated by the addition of a small quantity of a ferrous salt) and leads to the formation of a mixture of mannose and levulose. H. W.

**Oximes of Rhodoseose and Fucose.** E. VOTOČEK (*Zeitsch. Zuckerind. Böhm.*, 1919, **43**, 572—574).—*Rhodoseoxime*, m. p. 188—189°, is obtained in 97% yield by the action of Wohl's hydroxylamine solution on an aqueous solution of rhodoseose; *fucoseoxime* is similarly prepared, and has m. p. 188—189° when rapidly heated. When treated with acetic anhydride and sodium acetate, each oxime yields the same *acetylrhodoseonitrile*, m. p. 177—178°, whilst, in addition, a *substance*, m. p. 115—116°, which does not appear to be an acetyl-nitrile, is obtained as by-product from rhodoseoxime. *is*Rhodoseose, in sharp contrast to rhamnose, rhodoseose, and fucose, does not yield a sparingly soluble oxime. H. W.

**Action of Braun's Dihydrazine on certain Methyl-pentoses.** E. VOTOČEK (*Zeitsch. Zuckerind. Böhm.*, 1919, **43**, 574—577).—It has been shown by von Braun that diphenyl-

methanedimethylhydrazine does not react with ketonic sugars, but yields hydrazones with arabinose, rhamnose, galactose, and mannose, but not with xylose or dextrose; in a private communication to the authors he has suggested that this difference in behaviour of aldoses is connected with the spatial arrangement of the hydrogen and hydroxyl groups around the three asymmetric carbon atoms adjacent to the aldehydic group, and that when these groups occupy

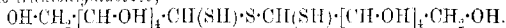


alternate positions (annexed formula) there is no tendency towards the formation of a hydrazone. This hypothesis has been tested and confirmed at the instances of rhodose, fucose, and *isorhodose*, since the former two readily give *hydrazones*, m. p. 218° and 221° (partial decomp.) respectively, whilst the last-named does not react with Braun's dihydrazine.

H. W.

**Thiodisaccharides from Galactose.** WILHELM SCHNEIDER and ANNEMARIE BEUTHER (*Ber.*, 1919, 52, [B], 2135—2149).—The observation that certain saccharoses react more readily with hydrogen sulphide in pyridine solution than does dextrose has led the authors to an extended examination of the behaviour of *d*-galactose in the hope of elucidating the constitution of the thio-derivatives.

When a solution of *d*-galactose in ice-cold pyridine is repeatedly saturated with dry hydrogen sulphide with exclusion of air and the product is worked up as already described in the case of dextrose (A., 1916, i, 791) and converted into the silver salt, a product is obtained which contains, as in the case of the dextrose derivative, more than one atom of sulphur for each atom of silver. During the course of the initial action, however, a crystalline *precipitate* is observed to separate, which has the composition  $\text{C}_{12}\text{H}_{20}\text{O}_{10}\text{S}_3\cdot 3\text{C}_5\text{H}_5\text{N}$ , and readily passes by loss of pyridine into *trithiodigalactose*,



The latter melts somewhat indefinitely between 139° and 142°, and is readily decomposed even by solution in water or aqueous pyridine. Protracted boiling with water converts it into galactose. The specific rotation could not be accurately determined on account of its instability; solutions in aqueous pyridine are initially laevorotatory, but rapidly change in sign, probably owing to a more or less complete hydrolysis of trithiogalactose to galactose. When an aqueous solution is treated with silver nitrate, silver sulphide is immediately precipitated, so that the isolation of a silver salt is impossible. Confirmation of the formula attributed to trithiodigalactose is found in its conversion into a *dodeca-acetyl* derivative, leaflets, m. p. 157°,  $[\alpha]_D^{20} + 24\cdot8^\circ$ , in acetylene tetrachloride solution.

The quantity of the crystalline compound which separates only corresponds with a small amount of the original material; further precipitations were therefore effected by the regulated addition of ether to the filtrate, whereby a *product*, needles, m. p. 183—184°, which has also the composition of a trithiodisaccharose, was isolated;

this is possibly either an isomeride or a disulphide oxidation product of trithiodigalactose.

The isolation of a trithiodisaccharose affords an obvious explanation of the high sulphur content of the thio-sugars and their silver salts.

The contrast between the stability of the sulphur atom in thioisotrehalose (Schneider and Wrede, A., 1917, i, 540) and the instability of trithiodigalactose has led the authors to prepare thio- and seleno-digalactose, which are found to be perfectly stable substances; thus *octa-acetylthiodi-d-galactose*, colourless, slender needles, m. p.  $200^{\circ}$ ,  $[\alpha]_D^{20} - 5.72^{\circ}$  or  $-6.08^{\circ}$ , in acetylene tetrachloride solution, is prepared by the interaction of bromoacetylgalactose on an alcoholic solution of potassium sulphide, and is transformed by methyl-alcoholic ammonia into *thiodi-d-galactose*,  $C_{12}H_{20}O_{10}S$ , colourless, pointed needles, m. p.  $230^{\circ}$ ,  $[\alpha]_D^{20} - 41.86^{\circ}$  in aqueous solution. The latter substance closely resembles thioisotrehalose in chemical properties; with mercuric chloride solution it yields a white precipitate,  $2HgS, HgCl_2$ . Similarly, *octa-acetylselenodigalactose* crystallises in small, colourless needles, m. p.  $202^{\circ}$ ,  $[\alpha]_D^{20} - 13.4^{\circ}$  or  $-12.5^{\circ}$  in acetylene tetrachloride, and is converted by methyl-alcoholic ammonia into *selenodi-d-galactose*, slender needles grouped in clusters, m. p.  $228^{\circ}$ ,  $[\alpha]_D^{20} - 36.6^{\circ}$  or  $-37.6^{\circ}$  in aqueous solution.

H. W.

**Action of Hydrogen Sulphide on Sugars. II.** WILHELM SCHNEIDER and OTTILIE STIEHLER (*Ber.*, 1919, 52, [B], 2131—2135).—A further study of the action of hydrogen sulphide on dextrose and other sugars in pyridine solution (compare Schneider, A., 1916, i, 791).

The proportion of sulphur which enters the dextrose molecule is found to increase with the duration of the action and with increasing concentration of hydrogen sulphide, so that it appears that the system tends towards an equilibrium between unchanged and thio-sugar, water and hydrogen sulphide. Under suitable conditions, the dextrose molecule can combine with considerably more than one atom of sulphur.

Among the hexoses, *d-galactose*, *d-mannose*, and *d-fructose* react considerably more rapidly with hydrogen sulphide than does dextrose and absorb more than one atom of sulphur for each molecule; the behaviour of *l-rhamnose* and *l-arabinose* is similar. Lactose and maltose, on the other hand, only react very slowly, whilst  $\alpha$ -methylglucoside and mannitol do not yield thio-compounds. The slight activity of penta-acetylglucose is probably due to the preliminary loss of one or more acetyl groups. The ability to yield thio-derivatives appears to depend on the presence of a reactive ketonic or aldehydic group in the molecule.

H. W.

**Action of Reducing Agents on the Chloraloses.** M. HANRIOT and ANDRÉ KLING (*Ann. Chim.*, 1919, [ix], 12, 129—150).—When the chloraloses are heated with ammonia in solution in perfectly dry methyl alcohol in sealed tubes at  $150^{\circ}$  for four to

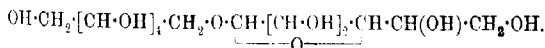
six hours, one of the three atoms of chlorine is replaced by hydrogen, giving products which the authors name dechlorochloraloses. With benzoyl chloride these compounds give dibenzoyl derivatives. Thus  $\beta$ -chloralose gives *dechloro- $\beta$ -chloralose*,  $C_8H_{12}O_6Cl_2$ , m. p.  $156-157^\circ$ ,  $[\alpha]_D -10.57^\circ$ , giving a *dibenzoyl* derivative;  $\alpha$ -chloralose gives *dechloro- $\alpha$ -chloralose*, m. p.  $165^\circ$ ,  $[\alpha]_D +9.96^\circ$ , giving a *dibenzoyl* derivative, m. p.  $146^\circ$ .  $\beta$ -Galactochloralose gives the compound,  $C_8H_{12}O_6Cl_2$ , occurring in two forms, one having m. p.  $96^\circ$ , the other m. p.  $133^\circ$ ; both have  $[\alpha]_D -29.20^\circ$ , and give a *dibenzoyl* derivative, m. p.  $116^\circ$ .  $\beta$ -Arabinochloralose gives the compound  $C_7H_{10}O_5Cl_2$ , m. p.  $88-89^\circ$ ,  $[\alpha]_D -19.72^\circ$ , giving a *dibenzoyl* derivative, m. p.  $90.5^\circ$ .

On oxidation with nitric acid dechloro- $\beta$ -chloralose gives a mixture of a lactone and an acid, from which, by the action of ammonia, *dechloro- $\beta$ -chloralamide*,  $C_7H_9O_5Cl_2 \cdot CO \cdot NH_2$ , m. p.  $161-162^\circ$ , is obtained. Under similar conditions dechloro- $\beta$ -galactochloralose on oxidation only yields mucic acid. Dechloro- $\beta$ -arabinochloralose yields an acid,  $C_7H_9O_5Cl_2$ , m. p.  $215^\circ$ .

When hydrolysed with hydrochloric acid the dechlorochloraloses simply split up, giving the sugar and dichloroacetaldehyde. The dechlorochloraloses may be more easily obtained, and with better yield, by the reduction of the corresponding chloralose with aluminium amalgam in neutral or acid aqueous alcoholic solution, or with a zinc-copper couple or zinc and sulphuric acid, or by electrolysis in acid solution. When reduced in alkaline solution, as by the action of sodium amalgam, the  $\alpha$ - and  $\beta$ -chloraloses derived from dextrose each lose two atoms of chlorine, yielding respectively *bidechloroglucos- $\alpha$ -chloralose*,  $C_8H_{12}O_6Cl$ , m. p.  $168^\circ$ , giving a *dibenzoyl* derivative, m. p.  $149^\circ$ ; and *bidechloroglucos- $\beta$ -chloralose*, m. p.  $166^\circ$ , giving a *dibenzoyl* derivative, m. p.  $146^\circ$ . On oxidation, the former of these two compounds gave oxalic and saccharic acids, whilst the second gave a *lactone*,  $C_7H_7O_5Cl$ , isolated as its *hydrate*,  $C_7H_7O_5Cl \cdot N_2H_4$ , m. p.  $170^\circ$ .

Attempts to remove the third atom of chlorine from the chloraloses by reduction were not successful. W. G.

**Catalytic Hydrogenation of Lactose.** J. B. SENDERENS (*Compt. rend.*, 1920, 170, 47-50). A repetition of Ipatiev's work on the catalytic hydrogenation of lactose in aqueous alcoholic solution in the presence of nickel and nickel oxide (compare A., 1913, i. 10). It is now shown that if the catalyst is only slightly active, the reaction ceases when the aldehyde group is reduced to the group  $\cdot CH_2OH$ , and the author has isolated the resulting compound, which he calls *lactositol*.



This compound has m. p.  $73^\circ$ ,  $[\alpha]_D +12.2^\circ$ , and crystallises with  $H_2O$ . On hydrolysis with dilute sulphuric acid it yields sorbitol and galactose.

If in the hydrogenation a more active catalyst is used, the action



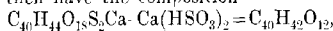
proceeds further, the acetal group being attacked, hydrolysis occurs, and the resulting products are dulcitol and sorbitol. W. G.

**Isolation of Inulin and Lævulose from Plant Sap.**  
ARNOLD DANIEL (D.R.-P. 313986; from *Chem. Zentr.*, 1919, iv, 665).—The process depends on the addition of strongly alkaline substances in the warm, whereby the harmful non-inulin substances are partly precipitated and partly converted into a harmless form; the concentration of the alkali is to be so chosen that a further precipitation does not occur on treatment of the sap. The preparation of inulin from dahlia tubers by means of alkali hydroxides, or carbonates, or alkaline earths is described. Pure inulin may also be converted into pure lævulose and other degradation products of inulin, such as caramel and dextrin.

H. W.

**Chemical Structure of the Lignin of Spruce Wood.**  
PETER KLASON (*Arkiv Kem. Min. Geol.*, 1917, 6, No. 15, 1—21).—Spruce wood has previously been shown to consist approximately of: 50% cellulose, 16% other carbohydrates, 30% lignin, and 4% of other substances. Since the "other carbohydrates" have become of great practical importance, the name "lignosans" is suggested for them.

The composition of lignin has previously been derived from a study of barium lignosulphonate and found to be  $C_{40}H_{40}O_{11}$  (compare A., 1908, i, 717, the composition then being wrongly given as  $C_{40}H_{42}O_{11}$ ). *Calcium lignosulphonate*,  $C_{40}H_{44}O_{18}S_2Ca$ , has now been prepared; it apparently contains one molecule more water than the barium salt, and gives a cryoscopic molecular weight of 1628—1753, so that it forms double molecules in aqueous solution. Lignin would then have the composition



that is, it results from the condensation of 1 mol. of coniferyl alcohol and 3 mols. of hydroxyconiferyl alcohol with the loss of 3 mols. of water. (This composition is apparently taken as preferable to that obtained from the barium salt.) *Naphthylamine lignosulphonate* is readily obtained as a yellow, sandy powder by precipitating a solution of the calcium salt with naphthylamine hydrochloride.

When the mother liquors, from which the above calcium salt has been precipitated, are heated with naphthylamine hydrochloride, a *naphthylamine lignosulphonate*,  $C_{60}H_{60}O_{14}S_2N_3$ , different from the above, is precipitated. This can be considered as made up of: 1 mol. of coniferyl alcohol, 1 mol. of hydroxyconiferyl alcohol, 1 mol. of caffeic acid, 2 mols. of  $H_2SO_3$ , and 3 mols. of naphthylamine, the condensation of the first three components taking place with the loss of 3 molecules of water. The lignin forming the basis of this salt would thus have the formula  $C_{20}H_{30}O_8$ , and contain two methoxy-groups. Assuming that the lignin of wood is made up of an equal number of molecules of the two above lignins, its formula would be  $C_{60}H_{68}O_{21}$ , with six methoxy-groups, and such a composition agrees very well with analytical data.

It is suggested that the condensations above mentioned take place between the hydroxyl of an allyl alcohol group and the phenolic hydroxyl in another molecule, and so on, lignin thus being built up on the same principle that holds for polysaccharides and albumins.

The reason for including caffeic acid in the building up of the lignin  $C_{29}H_{26}O_8$  is that an acid residue must be present to account for the third molecule of naphthylamine in the salt, the other two molecules being bound by the sulphurous acid. Plant products are often substituted benzene derivatives, the first position being occupied by allyl alcohol or acrylic acid residues, whilst the positions 3, 4, and 5 are occupied by hydroxyl or methoxyl groups; caffeic acid is such a derivative.

The results obtained by the dry distillation of wood are in agreement with the above deductions, and all known facts agree with the assumption that lignin from spruce wood results from the condensation of methylated hydroxycinnamyl alcohols or the corresponding aldehydes and acids, which are substituted similarly to protocatechuic acid.

Combinations of lignin and sulphite have the character of tannins, and lignin can be considered to be an insoluble tannin.

Investigation of the molecular weight of the above-mentioned calcium lignosulphonate by the ebullioscopic method gives the value 982 (theory, 916), so that at the boiling point it is not associated; the potassium salt gave similar results. Lignin prepared from spruce wood by digesting it with alcoholic sulphuric acid and removing the fat and resin with light petroleum gave a molecular weight of 650 in glacial acetic acid, as compared with the theoretical value 714 for  $C_{40}H_{42}O_{12}$ , that is, in agreement with the formula for the lignosulphonate.

Experiments on the behaviour of coniferin and coniferyl alcohol towards acid sulphites gave results in agreement with the assumption that lignin contains aromatic nuclei of the same structure as coniferyl alcohol, together with side-chains of the same constitution as allyl alcohol. The lignin reactions (compare A., 1908, i, 717), which are also given by calcium lignosulphonate after treatment with alkali, point to the same conclusion.

The final conclusion of the author is that lignin in wood is built up from pentoses, as the following equation, which gives dihydroxycinnamyl alcohol, indicates:  $2C_5H_{10}O_5 = C_9H_8O_3 + 5H_2O + CO_2$ . The methylation of the phenolic groups may be brought about by formaldehyde,  $R \cdot OH + CH_2O = R \cdot OCH_3 + O$ , the oxygen liberated then changing  $RH$  into  $R \cdot OH$ , and also oxidising allyl alcohol complexes into the corresponding aldehydes and acids, thus giving the complexes shown to be present in lignin.

T. S. P.

**Preparation of Hexamethylenetetramine Dinitrate.**  
 ZENTRALSTELLE FÜR WISSENSCHAFTLICH-TECHNISCHE UNTERSUCHUNGEN (D.R.-P. 298412; from *Chem. Zentr.*, 1919, iv, 498—499).—Solid hexamethylenetetramine is added, preferably with cooling, to

dilute aqueous nitric acid, which may contain sulphuric acid. Separation of the *salt* occurs so completely (about 95% of that theoretically possible) that the reaction may be applied immediately to the precipitation of nitric acid from its aqueous solution. H. W.

**Reduction of Methylene-blue by Glycine.** FRIEDRICH HASSE (*Biochem. Zeitsch.*, 1919, **98**, 159—177).—Glycine reduces methylene blue in alkaline solution. Other amino-acids do not give this reaction. Quantitative estimations show that acetaldehyde and dextrose give a weaker, creatine, catechol, and resorcinol an equal, and glucosamine and to a much greater extent adrenaline and quinol a higher reduction than glycine. These observations are discussed in relation to the Strecker-Traube reactions.

S. S. Z.

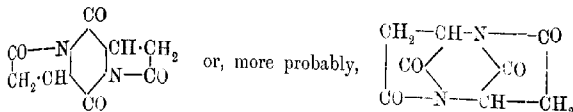
**Calcium Haloid Salts of Carbamide and Asparagine.** YUZURU OKUDA and KIOSHI FUJIIWAKA (*J. Tokyo Chem. Soc.*, 1919, **40**, 404—412).—Carbamide and asparagine form double compounds with calcium haloids, which are easily crystallised. Thus the compound,  $\text{CaI}_2 \cdot 6\text{CO}(\text{NH}_2)_2$ , m. p. 168—169°, hexagonal plates having a bitter taste, is obtained by passing hydrogen sulphide into a mixture of powdered calcium carbonate, iodine, and a little water until the iodine has dissolved, removing the excess of carbonate, and adding carbamide to the filtrate, which is then made slightly alkaline with lime water; the crystals are obtained by concentrating the solution, and are recrystallised from water or alcohol. Other compounds described are:  $\text{CaBr}_2 \cdot 6\text{CO}(\text{NH}_2)_2$ , m. p. 146°, hexagonal plates;  $\text{CaCl}_2 \cdot 4\text{CO}(\text{NH}_2)_2$ , hygroscopic, hexagonal crystals;  $\text{CaI}_2 \cdot \text{C}_4\text{H}_8\text{O}_3\text{N}_2 \cdot 4\text{H}_2\text{O}$ , m. p. 136°;  $\text{CaBr}_2 \cdot \text{C}_4\text{H}_8\text{O}_3\text{N}_2 \cdot 4\text{H}_2\text{O}$ ; and  $\text{CaCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_3\text{N}_2 \cdot 4\text{H}_2\text{O}$ , m. p. 67°, hygroscopic, columnar crystals.

CHEMICAL ABSTRACTS.

**Transformation of Asparagine into the Dipeptide of Aspartic Acid.** C. RAVENNA and G. BOSINELLI (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 113—117).—When ordinary *l*-asparagine is subjected to prolonged boiling in aqueous solution, it undergoes partial racemisation (compare Pringsheim, A., 1910, i, 303; ii, 437). From the inactive asparagine separable from the solution by crystallisation, the *d*-isomeride may be obtained pure by dissolving a little magnesium sulphate and potassium and calcium hydrogen phosphates in the 2% aqueous solution and leaving the latter exposed for fifteen days to the air at the ordinary temperature; the mould which develops on the liquid rapidly attacks the *l*-asparagine, and the *d*-asparagine may afterwards be crystallised out.

The mother liquors from the inactive asparagine yield no further crystals, but are found to contain the dipeptide of aspartic acid (asparagylaspartic acid) (compare Fischer and Koenigs, A., 1907, i, 486),  $\text{CO}_2\text{H} \cdot \text{CH}(\text{NH}_2) \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ . The latter may be purified by heating it in an open vessel for some hours

at 210°, this treatment converting it into *diketopiperazinediacetic anhydride*,



which neither melts nor decomposes at 320°; by baryta water in the cold this anhydride is transformed into asparagylaspartic acid.

In view of the widespread occurrence of asparagine in plants and the importance of the polypeptides in relation to the synthesis of proteins, it seems possible that the ready formation of the dipeptide of aspartic acid from asparagine may play a part in vegetable metabolism.

T. H. P.

**Transformation of Ammonium Malate into the Dipeptide of Aspartic Acid.** C. RAVENNA and G. BOSINELLI (*Atti R. Accad. Lincei*, 1919, [v], 28, ii, 137—139).—The composition and characters of diketopiperazinediacetic anhydride (compare preceding abstract) indicate the identity of this compound with that obtained by Dessaignes (Beilstein, 3rd edition, I, 1389) by heating ammonium hydrogen malate, and described in the older literature as fumaramide. The conversion of the latter compound into the dipeptide of aspartic acid by the action of baryta solution in the cold confirms the identity.

T. H. P.

**Chloroacetates of S-Alkylthiocarbamides.** JOHN TAYLOR (T., 1920, 117, 4—11).

**Equilibrium Conditions in the Bucher Process for the Fixation of Nitrogen.** J. H. FERGUSON and P. D. V. MAXING (*J. Ind. Eng. Chem.*, 1919, 11, 946—950).—In Bucher's process for the fixation of nitrogen the main reaction is represented by the equation  $2\text{Na}_2\text{CO}_3 + 4\text{C} + \text{N}_2 \rightleftharpoons 2\text{NaCN} + 3\text{CO}$ , the iron apparently acting only as catalyst. In order to ascertain the empirical relationships which may be taken as representing the probable conditions of equilibrium in practice, a stream of gas of varying composition was passed over the charge, which was heated in an iron boat and the amounts of carbonate converted into cyanide at the equilibrium points were estimated. It was found that the iron boat was not affected in experiments at 950° to 1000° in which the gas contained up to 80% of carbon monoxide. Curves were plotted showing the percentage formation of cyanide in relation to the proportion of carbon monoxide in the initial gas. The results indicated that the temperature has relatively little influence on the conversion when the gas contains little carbon monoxide, but would have much more influence in the case of gas, such as producer gas, containing, say, 30% of carbon monoxide. At 1000° it is possible to convert up to about 60% of the alkali carbonate by means of pro-

ducer gas, and the yield would be increased by the use of a higher temperature. The amount of conversion decreases with the rise in the proportion of carbon monoxide in the initial gas, and in the case of gas containing 60% of carbon monoxide only half of the carbonate is converted. The results also indicated that the initial reduction of the sodium carbonate to sodium is the controlling factor in the Bucher process, and that the effect of the carbon at this stage may be to maintain the pressure of the carbon dioxide below that of the dissociation pressure of the carbonate. This view received support from the results obtained by plotting the amounts of carbonate converted into cyanide in relation to carbon dioxide instead of carbon monoxide. [See, also, *J. Soc. Chem. Ind.*, 1920, 17A.]

C. A. M.

**Action of Mercuric Cyanide on Metallic Salts.** LILANANDA GUPTA (*T.*, 1920, 117, 67—73).

**Effect of Pressure, and of Dissolved Air and Water on the Melting Point of Benzene.** THEODORE W. RICHARDS, EMMETT K. CARVER, and WALTER C. SCHUMB (*J. Amer. Chem. Soc.*, 1919, 41, 2019—2028).—The freezing point of benzene and the effect of dissolved air and water on this quantity have been experimentally investigated. It is shown that benzene saturated with air under atmospheric pressure melts  $0.003^{\circ}$  below the true triple point. Benzene thus saturated has its freezing point but little altered by change of pressure. There appears to be no large amount of supersaturation. The effect of pressure in the absence of dissolved air is shown to alter the freezing point  $0.029^{\circ}$  per atmosphere. Saturation with water lowers the freezing point of benzene  $0.095^{\circ}$ . The true freezing point of benzene saturated with air is probably not far from  $5.493^{\circ}$  and the true triple point not far from  $5.496^{\circ}$ .

J. F. S.

**The Nitrotoluenes. III. Binary Systems of the Components: *p*-Nitrotoluene, 2:4-Dinitrotoluene, and 2:4:6-Trinitrotoluene.** JAMES M. BELL and CHARLES H. HERTY, JUN. (*J. Ind. Eng. Chem.*, 1919, 11, 1124—1128. Compare this vol., i, 22, 23).—The melting points of two-component systems of three of the principal nitration products of toluene have been determined by the cooling-curve method, and the complete results plotted in curves. The term "melting point" is defined as the temperature at which crystals first appear, and in determining it the question of super-cooling has to be taken into consideration, whilst the eutectic point is the temperature at which there is equilibrium between the solids and melted mass. The probable values found for the melting points were: For *p*-nitrotoluene (*MNT*),  $51.5^{\circ}$ ; 2:4-dinitrotoluene (*DNT*),  $69.6^{\circ}$ ; and 2:4:6-trinitrotoluene (*TNT*),  $80.35^{\circ}$ , in each case with a + or - error of  $0.3^{\circ}$ . In the binary system *MNT-TNT* the eutectic points were  $33.85-33.95^{\circ}$ ; in the system *DNT-TNT*,  $45.4-45.6^{\circ}$ ; and in the system *MNT-DNT*,  $26.44-26.54^{\circ}$ . In no instance did the free-

ing-point curves intersect at other than the eutectic temperature points, and the conclusions of Giua (A., 1914, i, 817) as to the existence of molecular compounds in these three cases were therefore not supported by these results.

C. A. M.

**The Nitrotoluenes. IV. The Three-component System: *p*-Nitrotoluene, 2:4-Dinitrotoluene, and 2:4:6-Trinitrotoluene.** JAMES M. BELL and CHARLES H. HERTY, Jun. (*J. Ind. Eng. Chem.*, 1919, 11, 1128—1130).—The freezing points of mixtures of these compounds have been determined and plotted in the conventional triangular diagrams, the primary freezing point being the temperature at which the first solid separated, the second that at which the second solid separated, and the eutectic point that at which all three solids were in equilibrium with the melted mass. The diagram thus consisted of three fields separated by three boundary curves, which intersected at the ternary eutectic point. No evidence was obtained pointing to the existence of binary molecular compounds as claimed by Giua (see preceding abstract). By a method of interpolation both the composition and temperature of points on the boundary curves may be found, and in this way it is possible to identify the composition of a mixture of the three compounds from the determination of the freezing points. C. A. M.

***p*-Cymene. III. Preparation of 2-Chloro-5:6-dinitro-*p*-cymene.** H. A. LUS and R. C. YOUNG (*J. Ind. Eng. Chem.*, 1919, 11, 1130—1133. Compare A., 1918, i, 339; 1919, i, 398).—The chief product formed in the nitration of 2-chloro-*p*-cymene is 2-chloro-5:6-dinitro-*p*-cymene, whilst an isomeric compound also appears to be formed. Another chlorodinitro-compound (m. p. 90–91°) containing less carbon than chlorodinitrocymene is also formed in small quantity, together with a substance of unknown composition, possibly a chloroterephthalic acid.

C. A. M.

**4-Chlorobenzene-1:3-disulphonic Acid and its Transformation into the Symmetrical Compound.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1919, 38, 351—355).—4-Chlorobenzene-1:3-disulphonic acid gives a *potassium* salt,  $C_6H_3Cl(SO_3K)_2 \cdot H_2O$ , a *barium* salt,  $C_6H_3Cl(SO_3)_2 \cdot Ba \cdot 4H_2O$ , and a *dichloride*,  $C_6H_3Cl(SO_2Cl)_2$ .

m. p. 90.5°.

When the anhydrous barium salt is heated with sulphuric acid, containing some sulphur trioxide, at 300° for five hours it is partly converted into 5-chlorobenzene-1:3-disulphonic acid.

W. G.

**The Structure of the Chlorobenzenedisulphonic Acid prepared according to D.R.-P. 260563.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1919, 38, 356—357).—By preparation and identification of its acid chloride it is shown that the acid obtained by the sulphonation of *p*-chlorobenzenesulphonyl chloride by the method of Meister, Lucius, and Brünig (D.R.-P. 260563) is 4-chlorobenzene-1:3-disulphonic acid.

W. G.

**Iodination of Aromatic Amines by means of Iodine and Persulphate.** K. ELLES and H. VOLK (*J. pr. Chem.*, 1919, [ii], 99, 269—275. Compare A., 1913, i, 841).—The success of this method when applied to aromatic amines and their acyl derivatives is very limited. The yields of 2-iodo-*p*-nitroaniline (*acetyl* derivative, needles, m. p. 128—130°) and 2:4-di-iodo-*o*-nitroaniline were good; of 2-iodo-*p*-toluidine and 2-iodosulphanilic acid, moderate; of 2:4-di-iodoaniline (accompanied by *p*-iodoaniline), *p*-iodoacetanilide, and 3-iodo-*p*-bromoaniline, poor. Indefinite products were obtained from *m*-xyldine, dimethylaniline, diphenylamine and its acetyl derivative, *p*-chloroaniline, *m*-bromoaniline, and *m*-nitroaniline, as well as from anisidine and phenacetin, although unpublished experiments with anisole and phenetole had given excellent results. Tribenzylamine was oxidised to benzaldehyde, and hexamethylenetetramine gave its additive di-iodide.

Except in the case of acetanilide, the acetic acid used in the earlier experiments was replaced by concentrated hydrochloric acid.

J. K.

**A New Modification of 3:4-Dinitromethylaniline.** HERBERT SWANN (T., 1920, 117, 1—4).

**Acylvanillylamides.** E. K. NELSON (*J. Amer. Chem. Soc.*, 1919, 41, 2121—2130).—Having shown capsaicin to be decenovanillylamide (compare A., 1919, i, 543), the author has prepared a number of acylvanillylamides and approximately determined their pungency. These amides are readily prepared by action on vanillylamine with the requisite acyl chloride. *Acetovanillylamide* has m. p. 84—85° (corr.);  $n_D$  1.550;  $n_D$  1.585;  $n_D$  1.655; *propiovanillylamide* has m. p. 108—110° (corr.);  $n_D$  1.495;  $n_D$  1.635;  $n_D$  1.680; *n-butyrovanillylamide* has m. p. 68—70° (corr.);  $n_D$  1.515;  $n_D$  1.580;  $n_D$  1.655; *isobutyrovanillylamide* has m. p. 118—120°;  $n_D$  1.465;  $n_D$  1.633;  $n_D$  1.635; *n-hexovanillylamide* could not be obtained crystalline; *n-heptovanillylamide* has m. p. 59—61° (corr.);  $n_D$  1.515;  $n_D$  1.595;  $n_D$  1.625; *n-octovanillylamide* has m. p. 41—43° (corr.);  $n_D$  1.56;  $n_D$  1.57; *n-nonovanillylamide* has m. p. 52°;  $n_D$  1.57;  $n_D$  1.59; *n-decovanillylamide* has m. p. 59—60°;  $n_D$  1.545;  $n_D$  1.555;  $n_D$  1.620; *n-undecovanillylamide* has m. p. 54—56°;  $n_D$  1.515;  $n_D$  1.540;  $n_D$  1.615; *n-dodecovanillylamide* has m. p. 60—61° (corr.);  $n_D$  1.52;  $n_D$  1.540;  $n_D$  1.60; *crotonovanillylamide* has m. p. 119—120° (corr.);  $n_D$  1.515;  $n_D$  1.605;  $n_D$  1.735; *undecenovanillylamide* has m. p. 53—55° (corr.);  $n_D$  1.55;  $n_D$  1.60;  $n_D$  1.63; *benzovanillylamide* has m. p. 140—142°;  $n_D$  1.590;  $n_D$  1.675;  $n_D$  1.695.

Below the *n*-hexoamide these substances have little or no pungency, but above this member the pungency increases rapidly with rise in molecular weight to the nonoamide and then diminishes again.

W. G.

**N-Methylvinylaniline.** JULIUS VON BRAUN and GEORG KIRSCHBAUM (*Ber.*, 1919, 52, [B], 2261—2265).—The substance is mainly of interest because it represents the first amine to be investi-

gated which contains the vinyl group directly united to the nitrogen atom.

Methyl- $\beta$ -bromoethylaniline is converted by trimethylamine into the quaternary bromide,  $\text{NMePh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_3\text{Br}$ , the bromine atom of which is not removed by protracted boiling with 51% potassium hydroxide solution; the corresponding quaternary base may, however, be obtained by the action of silver oxide, and, when heated under diminished pressure, yields *methylvinylaniline*; the success of the operation is dependent on the purity of the bromide. The freshly distilled base forms a colourless liquid with a sharp odour resembling that of formaldehyde or acetaldehyde. It has  $D_{25}^{25}$  0.9887. It differs from other anilines and bases in its instability and susceptibility to change; when preserved, even with exclusion of light, it gradually becomes more viscous; after 48 hours it has  $D_{25}^{25}$  1.0144, after 96 hours  $D_{25}^{25}$  1.0408, whilst after 144 hours it is too viscous to allow determination of density. When distilled, it boils mainly at  $98-99^\circ/16\text{ mm.}$ , but about one-third of the base is converted into a dark red, viscous mass, probably by the alkali of the glass. A further remarkable property is the ease with which the vinyl group is removed in the form of acetaldehyde by hydrolysing agents, the reaction occurring even with boiling water. For this reason, it has not been found possible to isolate pure salts or derivatives of the base.

The properties of methylvinylaniline throw doubt on the probability of the presence of the vinyl group attached to nitrogen in morphine, as has been postulated by Wieland and Kappelmeyer.

H. W.

**The Nitro-derivatives of Diphenylamine.** M. C. F. VAN DUIN and B. C. ROETERS VAN LENNEP (*Rec. trav. chim.*, 1919, **38**, 358—368).—An endeavour to determine the position of the last two nitro-groups in 2:4:6:3':?:?-hexanitrodiphenylamine, formed by nitrating 2:4:6:3'-tetranitrodiphenylamine in the cold (compare Austen, this Journ., 1875, 165).

2:4:6:2':4'-Pentanitrodiphenylamine, m. p.  $196-197^\circ$  (corr.), is easily prepared by saturating nitric acid ( $D\ 1.49$ ) with picrylaniline at a temperature not exceeding  $25^\circ$ .

2:4:6:2':4':6'-Hexanitrodiphenylamine may be prepared by nitrating picrylaniline in a nitric-sulphuric acid mixture or by nitrating pentanitrodiphenylamine at  $70^\circ$ . It has m. p.  $249^\circ$  (decomp.).

2:4:6:2'(?):3':4'-Hexanitrodiphenylamine, m. p.  $273-274^\circ$ , is obtained by nitrating the 2:4:6:3'-tetranitro-compound in a nitric-sulphuric acid mixture at the ordinary temperature. The nitro-group in the position 3' is very mobile; ammonia and the amines react immediately with it at the ordinary temperature. Thus dimethylamine gives *pentanitrodimethylaminodiphenylamine*, m. p.  $249^\circ$  (corr.).

2:4:6:3':4'-Pentanitrodiphenylamine, m. p.  $232^\circ$  (corr.), may be prepared by heating together picryl chloride and 3:4-dinitroaniline in a sealed tube at  $140^\circ$  for eight hours, and this may be



converted into the hexanitro-derivative, m. p. 273—274°, given above, thus establishing the position of the nitro-group at 4'.

In an endeavour to establish the position of the sixth nitro-group, 3:4:6-trinitrodimethylaniline was heated in alcoholic solution with aniline in a sealed tube at 120°, the product being 4:6-dinitro-3-anilinodimethylaniline, m. p. 143° (corr.). This was then nitrated, but, instead of the required pentanitrodimethylaminodiphenylamine, as described above, being obtained, the product was 2:4:6:2':4'-pentanitro-5-methylnitroaminodiphenylamine, m. p. 224—225° (corr.), which may also be prepared from 3-anilino-2:4:6-trinitrophenylmethylnitroamine, the intermediate product being 2:4:6:2'-tetranitro-5-methylnitroaminodiphenylamine, m. p. 200° (corr.).

By the action of *p*-nitroaniline on tetranitrophenylmethylnitroamine in boiling benzene solution, there is obtained a mixture of a compound, m. p. 235° (corr.), and 2:4:6:4'-tetranitro-5-methylnitroaminodiphenylamine, m. p. 200°. W. G.

**History of the Discovery of Oxonium Salts from Phenol Ethers.** F. KEHRMANN (*Ber.*, 1919, 52, [B], 2119).—The recent publication of Meyer and Gottlieb-Billroth (this vol., i, 37) on the action of nitric acid on phenol ethers leads the author to point out that the oxonium compound from thymol ethyl ether has been studied by Kehrman and Messenger (*Ber.*, 1901, 34, 1626), and its constitution has been elucidated by Decker and Solonina (*A.*, 1902, i, 767). H. W.

**Preparation of *p*-Phenetolecarbamide.** J. D. RIEDEL (D.R.-P. 313965; from *Chem. Zentr.*, 1919, iv, 738).—Solutions of alkali cyanides are treated successively with alkaline oxidising agents and phenetidinc hydrochloride; *p*-phenetolecarbamide separates immediately in good yield and in a highly pure condition. Sodium hypochlorite or sodium peroxide is cited as oxidising agent. H. W.

**Preparation of Acyl Derivatives of Cholic Acid.** J. D. RIEDEL (D.R.-P. 313413; from *Chem. Zentr.*, 1919, iv, 738—739).—*o*-Acetoxybenzoyl chloride is allowed to react with cholic acid in the presence of a substance which will combine with halogen acid. The product obtained from these substances in the presence of pyridine is a colourless, crystalline powder, insoluble in water, soluble in alcohol, m. p. 120°; it is tasteless and does not cause digestive disorders. It appears to be unchanged in the stomach, but to be readily dissolved in the intestines. It combines the pharmacological action of cholic and salicylic acids, and is expected to find application in pharmacy. H. W.

**Molecular Rearrangement in the Acylation of certain Aminophenols.** L. CHAS. RAIFORD (*J. Amer. Chem. Soc.*, 1919, 41, 2068—2080).—5-Bromo-3-amino-*p*-cresol, when acetylated, yielded 5-bromo-3-acetyl-amino-*p*-tolyl acetate, m. p. 169°, which, when hydrolysed, gave 5-bromo-3-acetyl-amino-*p*-cresol, m. p. 129°.

This compound, when benzoylated, yielded 5-bromo-3-benzoylamino-*p*-tolyl acetate, m. p. 172°, molecular rearrangement thus occurring. The constitution of the latter compound was proved by hydrolysing it, when 5-bromo-3-benzoylamino-*p*-cresol, m. p. 185°, was obtained identical with that prepared by benzoylating 5-bromo-3-amino-*p*-cresol by using 1 mol. of benzoyl chloride in ethereal solution with 2 mols. of the aminophenol.

A similar series of compounds was prepared from 4:6-dibromo-2-aminophenol. On acetylation, it yielded 4:6-dibromo-2-acetylaminophenylacetate, m. p. 199°, which, when treated with aqueous sodium hydroxide, gave 4:6-dibromo-2-acetylaminophenol, m. p. 174–175° (decomp.), and this with benzoyl chloride gave 4:6-dibromo-2-benzoylamino-phenyl acetate, m. p. 195–196°. This acetate, on saponification, gave 4:6-dibromo-2-benzoylamino-phenol, m. p. 198°, identical with that obtained by benzoylating 4:6-dibromo-2-aminophenol in dry ether.

In both these cases, therefore, the diacyl derivative always had the heavier benzoyl radicle attached to nitrogen, regardless of the order in which the radicles were introduced. As this is in direct opposition to the results obtained by Ransom and Nelson (compare A., 1914. i. 269), similar experiments were conducted with aminophenol itself, and, regardless of the order of introduction of the acyl radicles, the final product was 2-benzoylamino-phenyl acetate, m. p. 135°. Thus in these cases no differences have been observed between the behaviour, in this respect, of substituted and unsubstituted aminophenols, which indicates that acid-forming substituents are not responsible for the rearrangement. W. G.

**Halogenation. XIX. The Replacement of Sulphonic Groups by Chlorine and the Preparation of Organic Chloro-derivatives.** RASIK LAL DATTA and HARAPARBUTTY KUMAR MITTER (*J. Amer. Chem. Soc.*, 1919. **41**, 2028–2038).—When chlorine is passed into an aqueous solution of a sulphonic acid, the sulphonic group is readily replaced by chlorine, with very good yields. In some cases, additional chlorination also takes place. Aromatic substances which, in addition, contain an hydroxy-group exhibit a special facility for this displacement of the sulphonic group by chlorine, and the same has also been found true of amino-compounds, such as the nitroanilines. Under these conditions, *m*-isole- and phenetole-sulphonic acids yield tetrachloroketocyclohexadiene and some trichlorophenol. Phenolsulphonic acid gives trichlorophenol; *o*-cresol-5-sulphonic acid gives 5-chloro-*o*-cresol; *n*-cresol-6-sulphonic acid and *m*-cresol-2:6-disulphonic acid both give 2:6-dichloro-*m*-cresol; *p*-cresol-3-sulphonic acid gives a trichloro-*p*-cresol, m. p. 85–86°, which is either the 2:3:6- or the 1:5:6-trichloro-derivative; *p*-cresol-3:5-disulphonic acid gives 1:5-dichloro-*p*-cresol. Thymol mono- and di-sulphonic acids both give 2:5:6-trichlorothymol; carvacrol-5-sulphonic acid gives trichlorocarvacrol; oreinoldisulphonic acid gives pentachloro-oreinol 3:5-diketomethylpentachlorocyclohexane]. *o*- and *p*-Nitrophenol-sulphonic acids give, respectively, 4:6-dichloro-*o*-nitrophenol and

2:6-dichloro-*p*-nitrophenol; *o*- and *p*-nitroanilinesulphonic acids yield, respectively, 4:6-dichloro-*o*-nitroaniline and 2:6-dichloro-*p*-nitroaniline, whereas *m*-nitroanilinesulphonic acid does not give any definite product. Salicylic acid, on sulphonation and subsequent chlorination, gives 3:5-dichlorosalicylic acid. 2:4:6-Trisulpho-*m*-hydroxybenzoic acid gives the corresponding trichloro-derivative, and 3-sulpho-*p*-hydroxybenzoic acid yields 3:5-dichloro-*p*-hydroxybenzoic acid. W. G.

**Replacement of Sulphonic Groups by Nitro-groups by means of Nitrous Gases.** RASIK LAL DATTA and PHULDEO SAHAYA VARMA (J. Amer. Chem. Soc., 1919, **41**, 2039—2048).—The sulphonic acid groups in aromatic compounds may be very easily replaced by nitro-groups by means of nitrous gases. The action is generally effected in aqueous solutions, the nitrous gases being passed until saturation is reached. In the course of the action more nitro-groups frequently enter, with the formation of highly nitrated compounds. Many nitrations which cannot be brought about at all by nitric acid can be smoothly accomplished by this method. The reaction may be used for determining the constitution of nitro-compounds derived from known sulphonic acids. Aromatic compounds which are already substituted by hydroxy-groups or by halogens readily undergo replacement of the sulphonyl group by a nitro-group, in some cases more nitro-groups entering the ring in suitable positions. In the case of hydroxycarboxylic acids containing a sulphonyl group, both the sulphonyl and the carboxyl groups are replaced by nitro-groups. If, however, the compound does not already contain substituent halogens or hydroxyl groups, replacement of the sulphonyl group does not take place at all. Thus benzenesulphonic acid remains unacted on by treatment with nitrous gases.

By this method the following compounds have been prepared: 3:4-Dinitro-*o*-cresol from either *o*-cresol-3-sulphonic acid or *o*-cresol-4-sulphonic acid; 3:5-dinitro-*o*-cresol from the 3:5-disulphonic acid; 2:4:6-trinitro-*m*-cresol from either *m*-cresol-6-sulphonic acid or the 2:6-disulphonic acid; 3:5-dinitro-*p*-cresol from *p*-cresol-3-sulphonic acid; 3:5-dinitro-*o*-4-xyleneol from *o*-xyleneol-4-sulphonic acid; 5-nitro-*m*-4-xyleneol and 2-nitro-*p*-5-xyleneol from the corresponding sulphonic acids; 6-nitrothymol from thymolsulphonic acid; 2:4:6-trinitroresorcinol from either resorcinoldisulphonic acid, *m*-nitrophenolsulphonic acid, or *m*-hydroxysulphobenzoic acid; 2:4-dinitrophenol from either anisole- or phenetole-sulphonic acid; 2:4:6-trinitrophenol from the sulphonic acids of either *o*- or *p*-nitrophenol or *o*- or *p*-hydroxybenzoic acid. By direct sulphonation and subsequent treatment with nitrous gases without isolation of the sulphonic acid, 1:2:3-cresotic acid gave 3:5-dinitro-*o*-cresol; 1:3:4-cresotic acid gave 2:4:6-trinitro-*m*-cresol; 1:4:3-cresotic acid gave 3:5-dinitro-*p*-cresol; chloro-, bromo-, and iodo-benzenes gave the corresponding *p*-nitro-derivatives; phenylacetoneitrile gave *p*-nitrophenylacetoneitrile; and anthraquinone gave  $\beta$ -nitroanthraquinone. W. G.

**Preparation of Tetrahydro- $\beta$ -naphthol.** GEORG SCHROETER and WALTER SCHRAUTH (D.R.-P. 299603; from *Chem. Zentr.*, 1919, iv, 618).—Tetrahydronaphthalene- $\beta$ -sulphonic acid or its salts are fused with alkali. The acid is prepared by mixing tetrahydronaphthalene with a small excess of concentrated or absolute sulphuric acid; in the latter case the hydrocarbon dissolves immediately with spontaneous warming of the solution to 80–100°, and the process is completed by warming the mixture on the water-bath. On cooling, the mixture solidifies to a mass of crystals, from which the sulphonic acid can be isolated by pressure; alternatively, the alkali salts may be obtained by neutralising the slightly diluted mixture with alkali hydroxide and cooling, or may be salted out with potassium or sodium chloride. In addition, the alkali salts are prepared by the hydrolysis of tetrahydronaphthalene- $\beta$ -sulphonyl chloride (from the hydrocarbon and chlorosulphonic acid). When fused with potassium or sodium hydroxide, either singly or together or with addition of milk of lime, tetrahydronaphthalene- $\beta$ -sulphonic acid or its alkali salts are smoothly transformed, at 230–300°, into tetrahydro- $\beta$ -naphthol, silky needles, m. p. 59–60°, b. p. 145–146°/13 mm., 275–276°/760 mm., which is readily soluble in alkali hydroxide, in solutions of salts of the fatty and sulpho-fatty acids, and in concentrated sulphuric acid. The soap solutions remain permanently clear when diluted with conductivity water, whilst the naphthol is again precipitated when the sulphuric acid solutions are diluted. When the sulphuric acid solution is warmed, tetrahydro- $\beta$ -naphthol- $\alpha$ -sulphonic acid is formed, and crystallises when a small quantity of water is added to the solution; it is converted into a dinitrotetrahydronaphthol, yellow prisms, m. p. 112–114°, when treated in aqueous solution with concentrated nitric acid. Tetrahydro- $\beta$ -naphthol is intended to serve by itself or as starting material in the preparation of drugs, disinfectants, tanning materials, dyes, and explosives.

H. W.

**Tautomerism of Phenols. I. Quinol.** WALTER FUCHS and BENNO EISNER (*Ber.*, 1919, 52, [B], 2281–2286).—It is found in the case of quinol that phenols can react with sodium hydrogen sulphite in their tautomeric form as unsaturated cyclic ketones.

Reaction slowly occurs when an aqueous solution of quinol and sodium hydrogen sulphite is heated at the temperature of boiling water, whereby sodium cyclohexane-1:4-diol-1:2:4-trisulphonate, colourless needles, is formed. The sulphonic character of the product follows from the failure to obtain more than traces of sulphur dioxide from it by the action of mineral acids. The constitution of the substance is deduced from its oxidation by permanganate to succinic, oxalic, and, possibly, malic acids. cyclohexane-1:4-diol-1:2:4-trisulphonic acid could not be isolated in the pure condition; the specimens obtained consisted of a colourless, unstable material, m. p. 172–175° (decomp.), after previous darkening. The sodium salt can be used as a photographic developer; the possibility of its presence in the ordinary quinol developer is discussed.

H. W.

**Primary Aromatic Alcohols.** J. ALTWEGG (U.S. Pat. 1315619).— $\beta$ -Phenylethyl alcohol, b. p.  $89^{\circ}/4$  mm., is obtained in nearly theoretical yield by adding ethylene oxide (1 mol.) to an ethereal solution of magnesium phenyl bromide (1 mol.) at  $0^{\circ}$ , maintaining the temperature below  $10^{\circ}$  during the addition, then adding dry benzene, removing the ether by distillation, adding dilute sulphuric acid after cooling, and separating the phenylethyl alcohol from the benzene by decantation.

$\beta$ -p-Tolyethylethyl alcohol, b. p.  $98^{\circ}/3$  mm., is similarly obtained from magnesium p-tolyl bromide.  $\beta$ -p-Methoxyphenylethyl alcohol, b. p.  $121^{\circ}/5$  mm., is prepared with the aid of toluene instead of benzene.  $\beta$ -3-Methoxy-p-tolyethylethyl alcohol, similarly prepared, is a colourless oil, b. p.  $129^{\circ}$ – $130^{\circ}/5$  mm., with a faint, aromatic odour.

CHEMICAL ABSTRACTS.

**A New Sterol.** TAKEO IKEGUCHI (*J. Biol. Chem.*, 1919, 40, 175–182).—The author has previously described a sterol which he isolated from *Lycoperdon gemmatum* (A., 1915, i, 240). He has now obtained a similar product from other fungi, namely, *Armillaria edodes*, *Hydnum asparatum*, and *Collybia shiitake*. The crystalline sterols obtained from these sources melt at  $159^{\circ}$ – $160^{\circ}$ , have  $[\alpha]_D^{20} = -129.23^{\circ}$  to  $-129.55^{\circ}$ , and the formula  $C_{30}H_{48}O_2$ . They all give the same colour reactions, which differ slightly from those characteristic for cholesterol. As the author considers these crystals represent a sterol which is present in fungi generally, he proposes to call it *mycosterol*. Mycosterol inhibits the hæmolytic action of saponin, but not so powerfully as does cholesterol. It gives a crystalline compound with digitonin,  $C_{85}H_{142}O_{30}$ , m. p.  $242^{\circ}$  (decomp.). Mycosterol acetate,  $C_{32}H_{50}O_3$ , has m. p.  $169^{\circ}$ . Attempts to brominate failed, so that the molecule appears to be a saturated one.

It was not found possible to prepare a phenylhydrazone, so that it would appear likely that the two oxygen atoms are both present as hydroxyl groups. Only one of these is, however, acetylated by treatment with acetic anhydride, so that the other might possibly be existent as a tertiary alcohol grouping. To gain information on this point the oxidation products of the sterol were examined. On treatment with chromic acid in acetic acid solution mycosterol yielded an oxidation product,  $C_{30}H_{48}O_3$ , m. p.  $188^{\circ}$ – $189^{\circ}$ . Since this substance is neutral, it is concluded that a third hydroxyl group has been formed during the oxidation,  $C_{31}H_{46}(OH)_3 \rightarrow C_{31}H_{45}(OH)_3$ . Acetylation of the oxidation product confirmed this view, for a triacetate,  $C_{36}H_{54}O_6$ , needles, m. p.  $201^{\circ}$ – $202^{\circ}$ , was obtained.

J. C. D.

**Synthesis in the Naphthalene Nucleus.** A. MADINAVEITIA and J. PUYAL (*Anal. Fis. Quim.*, 1919, 17, 125–129).—The synthesis of 4-methoxy- $\alpha$ -naphthylcarbinol is described. A current of dry hydrogen chloride was passed into a mixture of  $\alpha$ -naphthyl methyl ether and anhydrous hydrogen cyanide in ethyl ether solution in presence of powdered zinc chloride. The precipitate formed

gave the aldehyde,  $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{CHO}$  (1.4), on boiling with water. This is a liquid (b. p.  $210\text{--}220^\circ/25\text{ mm.}$ ). On treatment with aqueous potassium hydroxide a mixture of 1-methoxy-1-naphthyl-*carbinol* (m. p.  $35^\circ$ ) and 1-methoxy-4-naphthoic acid (m. p.  $230^\circ$ ) was obtained. 4-Methoxy- $\alpha$ -naphthyl chloromethyl ketone,  $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , is synthesised by the action of anhydrous aluminium chloride on a mixture of  $\alpha$ -naphthyl methyl ether and chloroacetyl chloride in carbon disulphide solution; it forms needles, m. p.  $70^\circ$ . The corresponding *ethoxy*-derivative obtained in a similar way has m. p.  $98^\circ$ , and when heated with hydrochloric acid in a sealed tube at  $120^\circ$  yields  $\alpha$ -naphthyl chloromethyl ketone, which after recrystallisation from alcohol has m. p.  $130^\circ$ .

W. S. M.

**Preparation of Ethylidene Esters.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 313696; from *Chem. Zentr.*, 1919, iv, 661--665).—Organic vinyl esters or mixtures of vinyl esters are heated, in the presence or absence of a catalyst, with organic or inorganic acids, under conditions in which a molecule of the acid combines with a molecule of the ester and either at the ordinary or increased pressure until the action is complete. Thus, ethylidene diacetate is obtained by boiling vinyl acetate with acetic acid in the presence of a small quantity of concentrated sulphuric acid. *Vinyl benzoate*, b. p.  $203^\circ$ ,  $D_{20}^{20}$  1.065, and dry hydrogen chloride yield *chloroethyl benzoate*, b. p.  $134^\circ/20\text{ mm.}$ ,  $D_{20}^{20}$  1.172. Vinyl acetate forms *ethylidene acetate benzoate*,  $\text{CH}_3\cdot\text{CH}(\text{OAc})\cdot\text{OBz}$ , with benzoic acid and *chloroethyl acetate*,  $\text{OAc}\cdot\text{CHClMe}$ , with hydrogen chloride. The products are generally liquid, and excellent solvents for natural and artificial resins and cellulose nitrates and acetates; they may also be used in the preparation of varnishes, films, and impregnating mixtures.

H. W.

**Physiological Formation of Adrenaline and Syntheses of Phenylserine.** F. KNOOP (*Ber.*, 1919, 52, [B], 2266--2269).—The author criticises the views which have recently been advanced by Rosenmund and Dornsaft (this vol., i, 56) on the physiological formation of adrenaline, and points out that the production of many of the intermediate substances which they postulate is not in accordance with known physiological chemical process.

[With TOWMI.]—With the object of preparing *N*-methylserine,  $\alpha$ -chloro- $\beta$ -phenyl-lactic acid was added to a solution of methylamine; contrary to expectation, the product proved to be  $\beta$ -methylamino- $\alpha$ -hydroxy- $\beta$ -phenylpropionic acid, long prisms, decomposing completely at  $272^\circ$  after slowly darkening at  $250^\circ$ ; since the original acid contains the hydroxyl group in the  $\beta$ -position, it follows that it must have migrated to the  $\alpha$ -carbon atom probably owing to the intermediate formation of phenylglycidic acid. The constitution of the new acid is deduced from its oxidation by barium permanganate to  $\alpha$ -methylamino- $\alpha$ -phenylacetic acid, pointed prisms which sublime without melting at  $270^\circ$ . The latter acid is also obtained by the

action of methylamine on  $\alpha$ -chloro- $\beta$ -acetyl- $\beta$ -phenyl-lactic acid, short, coarse prisms, m. p. 131°. H. W.

**Alkamine Esters of Aminotoluic Acids and Similar Compounds.** E. A. WILDMAN (U.S. Pat. 1317251).— $\beta$ -Diethylaminoethyl 3-amino-*p*-toluate is obtained by reducing with tin, alcohol, and hydrochloric acid at 35° the product of reaction of  $\beta$ -diethylaminoethyl alcohol (1 mol.) and 3-nitro-*p*-toluoyl chloride (1 mol.), removing the tin with hydrogen sulphide, and precipitating the oily ester with sodium carbonate. It forms a *hydrochloride*, colourless crystals, m. p. 157–158°. The *dimethylaminoethyl* ester (*hydrochloride*, m. p. 139–140°) and various other alkamine esters of aminotoluic acids may be prepared similarly. They act as local anæsthetics, having but slight irritating or toxic action.

## CHEMICAL ABSTRACTS.

**Trimorphism of *allo*Cinnamic Acids.** A. W. K. DE JONG (Vers. Akad. Wetensch. Amsterdam, 1919, 27, 1219–1231).—The residue obtained by evaporating a dilute solution of either of the *allocinnamic* acids, m. p. 58° and 68°, yields the acid, m. p. 42°, at the ordinary temperature, but this acid is never obtained when concentrated solutions of the former two are used at the ordinary temperature. Aqueous solutions of the acids, m. p. 58° and 68°, yield only the acid, m. p. 58°, at –10°, but yield either of the acids at –16°. Freezing experiments, with special precautions to prevent inoculation by nuclei, were also performed, and the conclusion is drawn that the three *allocinnamic* acids are trimorphous forms.

## CHEMICAL ABSTRACTS.

**Anæsthetic Alkamine Esters of Alkyloxyaminobenzoic [Aminoalkyloxybenzoic] Acids.** E. A. WILDMAN (U.S. Pat. 1317250).—These esters, having properties similar to those of the esters described above, are prepared in an analogous manner. *Aminoethyl maminonisate* is an oil which forms a *hydrochloride*, m. p. 160°.

## CHEMICAL ABSTRACTS.

**Salosalicylide and the Polymeric Salicylides.** G. SCHROETER (Ber., 1919, 52, [B], 2224–2227).—The salicylides, which have hitherto been described by Anschütz, in particular that obtained by crystallisation from chloroform, show a varying molecular weight, since cryoscopic determinations in phenol or nitrobenzene indicate the formula  $(C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix})_4$ , and ebullioscopic determinations in chloroform or nitrobenzene indicate  $(C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix})_2$ ; the author now describes the preparation of a salicylide which undoubtedly has the constitution  $C_6H_4 \begin{smallmatrix} \diagup CO \cdot O \\ \diagdown O \cdot CO \end{smallmatrix} C_6H_4$ , and is therefore analogous to the dianthranilide obtained by Schroeter and Eisleb (A., 1909, i, 575). The immediate cause of publication is the recent

communication of Anschütz (this vol., i, 48) on a new disalicylide, which in many respects appears to be identical with the author's salosalicylide, although slight discrepancies are shown in the m. p. of the two substances and of their derivatives.

Salicylosalicylic acid, in spite of the presence of the free phenolic hydroxy-group, is smoothly converted by thionyl chloride into *salicylosalicylyl chloride*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ , m. p.  $99^\circ$ , which is converted in the usual manner into the corresponding *anilide*, long needles, m. p.  $160.5^\circ$ , *p*-*phenetidine*, m. p.  $154^\circ$ , *methyl ester*, m. p.  $88^\circ$ , and *glycine ester*, m. p.  $90-91^\circ$ ; the latter substance is readily hydrolysed, and, on further treatment with alkali, yields salicylic and salicyluric acid or *ethyl salicylurate*,  $\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , needles, m. p.  $88^\circ$ . Salosalicylide is most conveniently prepared by boiling salicylosalicylyl chloride dissolved in benzene with diethylamine; the dried, crystalline product has m. p.  $234^\circ$  when rapidly heated, but, after crystallisation from nitrobenzene, the m. p. is constant at  $214-217^\circ$ , whilst from benzene, a product, m. p.  $204-208^\circ$ , is obtained, the cause of these variations being unexplained. Cryoscopic and ebullioscopic determinations of the molecular weight in nitrobenzene and cryoscopic determinations in phenol show the substance to have the formula  $\text{C}_{14}\text{H}_{10}\text{O}_4$ .

A series of comparative experiments with salosalicylide and the so-called "chloroform-salicylide" (tetrasalicylide) is described, in all of which the latter behaves as the more stable substance. Thus, salosalicylide is converted by boiling glacial acetic acid into salicylosalicylic acid, whilst "chloroform-salicylide" remains unchanged. Similarly, the former rapidly yields methyl salicylosalicylate with methyl-alcoholic hydrogen chloride, whilst the latter is unaffected. Salicylosalicylanilide and salicylosalicyl-*p*-phenetidine are immediately obtained from salosalicylide and the requisite amine, whereas "chloroform-salicylide" can be boiled for hours with aniline without suffering alteration. Methyl alcohol containing sodium methoxide converts both salicylides into methyl salicylate. Concentrated sulphuric acid, alone and also in the presence of nitrobenzene, converts salicylosalicylic acid, salosalicylide, and "chloroform-salicylide" into salicylic acid; if the action is rapidly interrupted, it is found that the free acid is most rapidly, the "chloroform-salicylide" least rapidly, affected. Acetic anhydride and sulphuric acid convert salicylosalicylic acid into acetylsalicylosalicylic acid, the same product being mainly formed from salosalicylide; "chloroform-salicylide," however, yields *acetyltetrasalicylic acid*.

$\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , m. p. about  $120^\circ$ . Concentrated nitric acid converts salosalicylide into nitrosalicylic acid; under analogous conditions, chloroform-salicylide is but little affected, but nitration occurs with a mixture of nitric and sulphuric acids, *nitrosalicylide*,  $\left(\text{NO}_2\cdot\text{C}_6\text{H}_3\cdot\text{C} \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} \right)$  m. p.  $265^\circ$ , being formed. Protracted action of nitric acid on "chloroform-salicylide" in the presence of nitrobenzene leads to the formation of a *nitrotetrasalicylic acid*.



*Methyl tetrasalicylate* is obtained as an uncrystallisable, viscous, yellow mass by the action of salicylosalicylyl chloride on the sodium compound of methyl salicylosalicylate; the possible conversion of the ester into a tetrasalicylide has not yet been fully studied.

H. W.

**Phthalic Anhydride. II. The Melting Point of Pure Phthalic Anhydride. The System: Phthalic Anhydride-Phthalic Acid.** K. P. MONROE (*J. Ind. Eng. Chem.*, 1919, 11, 1116—1119).—Pure phthalic anhydride was prepared by subliming the product obtained by the oxidation of naphthalene in a vacuum apparatus in the presence of phosphoric oxide. The melting points of the first and second sublimates agreed. Phthalic acid was estimated by a method of differential titration, in which the sample was dissolved in acetone and the solution titrated with standard normal potassium phthalate with bromophenol-blue (tetra-bromophenolsulphonephthalein) as indicator. The sublimed preparations contained less than 0.1% of phthalic acid. The melting point was determined in a double-walled glass vessel immersed in a bath of sulphuric acid, and, after fusion, the temperature was gradually lowered to the point of incipient crystallisation. The equilibrium point of crystals and liquid was 130.84°. Mixtures of phthalic anhydride and acid tested in the same apparatus gave a eutectic temperature of 129.74°. By graphical interpolation, the melting point of pure phthalic acid was indicated to be 208°±2°. [See, further, *J. Soc. Chem. Ind.*, 1920, 57A.]

C. A. M.

**Phthalic Anhydride. III. The System: Naphthalene-Phthalic Anhydride.** K. P. MONROE (*J. Ind. Eng. Chem.*, 1919, 11, 1119—1120).—The freezing points of mixtures of pure naphthalene and phthalic anhydride were determined by the method previously described (preceding abstract), the eutectic point (26.9°) corresponding with 29.0% of phthalic anhydride. There was no evidence of the existence of solid solutions. The freezing points on the phthalic anhydride curve were calculated by means of the formula  $C = (-T_0 T \log_{10} x) / \Delta t$ , where  $C$  is a constant,  $x$  the mol. fraction of anhydride in the mixture,  $T_0$  the freezing point of pure phthalic anhydride,  $T$  the freezing point of the mixture, and  $\Delta t = T_0 - T$ . The calculated values of  $C$  in this equation, based on the experimental values of  $T$ , averaged 1190. And since  $L = RC / 0.4343$ , where  $L$  represents the molar heat of fusion of naphthalene (4560 cal.) and  $R$  the gas constant (1.9852 cal. per degree), the molar heat of fusion of phthalic anhydride = 5480 cal.

C. A. M.

**Phloroacetophenone.** KIEMUD BEHARI SEN and PRAPRULLA CHANDRA GHOSH (*T.*, 1920, 117, 61—63).

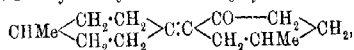
**Reactivity of Diphenylketen with the Nitrile Group.** ADOLFO GONZÁLEZ (*Anal. Fis. Quím.*, 1919, 17, 130—135).—Diphenylketen was mixed in sealed exhausted tubes with various

substances containing the group  $\cdot\text{C}\equiv\text{N}$ . After remaining for twenty-four or forty-eight hours at  $30^\circ$  or  $60^\circ$ , the contents of the tubes were dissolved in aqueous ether. The ether then evaporated, and the residue dissolved in alcohol. This solution of diphenylacetic acid, formed by the action of the water on the residual diphenylketen, was titrated with barium hydroxide solution. The nitriles of acetic, benzoic, and toluic acids showed only a feeble reaction with diphenylketen in the order named. Experiments with cinnamionitrile, ethylcarbamine, dimethylcyanamide, and diethylcyanamide showed that these substances also reacted to a small extent only. With cyanogen bromide, a dense liquid was obtained, after evaporation of the excess of cyanogen bromide, which yielded a yellow polymerisation product of diphenylketen. Hydrogen cyanide and cyanogen itself did not react with diphenylketen.

W. S. M.

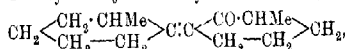
**Some New Bicyclic Ketones.** MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1919, 169, 1168—1171).—Using the method previously described (A., 1919, i, 447) with calcium hydride, the authors have prepared the following bicyclic ketones.

4'-Methyl-1:1'-cyclohexylidene-3-methylcyclohexan-6-one,



b. p.  $185^\circ/50$  mm.,  $D^{20}_D$  0.9659,  $n^{20}_D$  1.4963, gives an *oxime*, m. p.  $35^\circ$ , and, on reduction with hydrogen in the presence of platinum, sing Vavon's method, gives p-methylcyclohexyl-3-methylcyclohexan-6-one,  $\text{C}_7\text{H}_{12}\cdot\text{C}_7\text{H}_{11}\text{O}$ , b. p.  $170\text{---}175^\circ/50$  mm.,  $D^{24}_D$  0.947,  $n^{20}_D$  1.4852, yielding an *oxime*, m. p.  $123\text{---}124^\circ$ .

2'-Methyl-1:1'-cyclohexylidene-3-cyclohexan-2-one,



b. p.  $175^\circ/40$  mm.,  $D^{20}_D$  0.9926,  $n^{20}_D$  1.500, gives an *oxime*, b. p.  $160\text{---}165^\circ/20$  mm., and a *semicarbazone*, m. p.  $177\text{---}178^\circ$ . On reduction by Vavon's method, it yields 2'-methyl-1:1'-cyclohexyl-3-methylcyclohexan-2-one, b. p.  $166\text{---}169^\circ/35$  mm.,  $D^{20}_D$  0.9748,  $n^{20}_D$  1.4974, giving an *oxime* difficult to purify. Either of these ketones when reduced by sodium in absolute alcohol yields 2-methylcyclohexyl-3-methylcyclohexan-2-ol, b. p.  $165\text{---}168^\circ/40$  mm.,  $D^{20}_D$  0.973,  $n^{20}_D$  1.5034, giving an *allophanate*, m. p.  $223^\circ$ .

2' : 4'-Dimethyl-1:1'-cyclohexylidene-3:5-dimethylcyclohexan-2-

one,  $\text{CHMe} \begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array} > \text{C} : \text{C} \begin{array}{c} \text{CO} \text{---} \text{CHMe} \\ \text{CH}_2 \text{---} \text{CHMe} \end{array} > \text{CH}_2$ , b. p.  $184\text{---}185^\circ/40$  mm.,  $D^{20}_D$  0.956,  $n^{20}_D$  1.493, gives an *oxime*, an oil, and when reduced by sodium in absolute alcohol yields 2' : 4'-dimethyl-1:1'-cyclohexyl-3:5-dimethylcyclohexan-2-ol, b. p.  $183\text{---}191^\circ/40$  mm.,  $D^{20}_D$  0.945,  $n^{20}_D$  1.496, giving an *allophanate*, m. p.  $232^\circ$ . W. G.

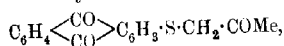
**The Constitution of Dypnopinacone and its Derivatives.**

MAURICE DELACRE (*Ann. Chim.*, 1919, [ix], 12, 150—178. Compare A., 1914, i, 1068; 1916, i, 679).—This paper, which should really

precede the theoretical paper previously published (compare A., 1918, i, 539), deals with the inter-relationship and preparation of the isomeric homodypnopinacones and homodypnopinacolins and their transformations. It is an elaboration of work previously published (compare A., 1896, i, 591, 662). W. G.

**Chlorothiolanthraquinones.** K. FRIES and G. SCHÜRMANN (*Ber.*, 1919, 52, [B], 2170—2181).—A continuation of previous work (A., 1912, i, 1005).

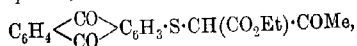
*Derivatives of 2-Thiolanthraquinone* [with K. Ross].—2-Aminoanthraquinone is diazotised in concentrated sulphuric acid solution and the diazonium sulphate is converted by potassium ethyl xanthate into *ethyl 2-anthraquinonylxanthate*, yellow needles, m. p. 151°, from which 2-thiolanthraquinone (Gattermann, A., 1912, i, 998) is obtained by the action of alcoholic potassium hydroxide solution. 2-Chlorothiolanthraquinone, yellow, prismatic crystals, m. p. 136°, is obtained by chlorination of the corresponding thiol or disulphide in chloroform solution, and is a highly reactive substance; with alcoholic potassium hydroxide solution it appears to yield a solution of potassium 2-anthraquinonesulphenate, but the corresponding acid could not be isolated. When boiled with acetone it gives 2-acetylthiolanthraquinone,



yellow prisms, m. p. 165°, whilst with aniline in benzene or chloroform solution it forms 2-anilinothiolanthraquinone, orange needles, m. p. 171°. When a solution of the chlorothiol in chloroform is shaken with water it gives 2-anthraquinonesulphenic anhydride, small, colourless crystals, m. p. 260° (decomp.), which is also produced when the chloride is boiled with alcohol.

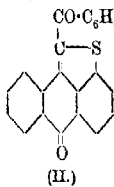
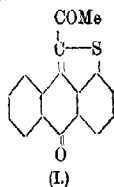
*Derivatives of 1-Thiolanthraquinone.*—Di-1-anthraquinonyl disulphide (compare Gattermann, *loc. cit.*) is most conveniently prepared by treatment of an alcoholic solution of 1-chloroanthraquinone with aqueous sodium disulphide, and is transformed into the corresponding thiol by the action of dextrose and sodium hydroxide.

1-Bromothiolanthraquinone reacts readily with ammonia, aniline, and dimethylaniline respectively, yielding the corresponding amide, orange needles, which do not melt below 300° and are converted by boiling acetic acid into *peri*-anthraquinone-1:9-thiazole (Gattermann, *loc. cit.*), *anilide*, shining, red needles, m. p. 210°, and *p*-dimethylaminophenyl derivative, red needles, m. p. 285°. With ethyl sodioacetoacetate, 1-bromothiolanthraquinone yields the compound,



yellow needles, m. p. 163°, which when boiled with mineral acid passes into the substance (I), yellow, prismatic crystals, m. p. 175°. Similar ring formation occurs when an alkali salt of 1-thiolanthraquinone is treated with *w*-chloro-*p*-hydroxyacetophenone, the *peri*

duct (II) crystallising in golden leaflets, m. p. 258°, and yielding a red sodium salt. On the other hand, sodium 1-anthraquinone-



sulphenate reacts normally with *p*- and *o*-nitrobenzyl chlorides, yielding 1-anthraquinonyl *p*-nitrobenzyl sulphide, orange leaflets, m. p. 243°, and 1-anthraquinonyl *o*-nitrobenzyl sulphide, orange needles, m. p. 251°; attempts to eliminate water from these compounds with the formation of a thiophen ring were unsuccessful. Resorcinol and 1-bromothiolanthraquinone gave 1-anthraquinonyl 4-resorenyl sulphide, orange needles, m. p. 232°.

1-Anthraquinonyl phenyl sulphide, m. p. 185°, is formed by the action of benzene on 1-chlorothiolanthraquinone in the presence of aluminium chloride, and is identical with the product obtained by Gattermann (*loc. cit.*) from *α*-nitroanthraquinone and phenyl mercaptan.

The action of ethyl sulphate on an aqueous-alcoholic solution of sodium anthraquinonesulphenate leads to the formation of 1-anthraquinonyl ethyl sulphoxide, yellow needles, m. p. 180° (decomp.), the constitution of which follows from its conversion by acetic and hydrobromic acids into 1-anthraquinonyl ethyl sulphide, m. p. 183° (Gattermann, *loc. cit.*); on the other hand, the free acid, when suspended in alcohol and treated with ethyl sulphate, is transformed into the corresponding ethyl ester, m. p. 149° (Fries, *loc. cit.*).

H. W.

**4-Aminoanthraquinone-1-sulphenic Acid.** K. FRIES and J. SCHÜRMANN (*Ber.*, 1919, 52, [B], 2182—2195).—The only sulphenic acid which has hitherto been isolated in the pure condition is 1-anthraquinonesulphenic acid (Fries, A., 1912, i, 1005); in their endeavour to isolate further examples of this class of substance the authors now describe attempts to prepare the corresponding 4-hydroxy-, 4-methoxy-, and 4-amino-compounds, which, however, are not entirely successful.

4-Bromo-1-hydroxyanthraquinone, coarse, orange-yellow needles, m. p. 197°, is prepared by the action of bromine on a hot solution of 1-hydroxyanthraquinone in glacial acetic acid in the presence of sodium acetate. (It forms a red sodium salt, which is sparingly soluble in water.) Under similar conditions, but with double the amount of bromine, 2,4-dibromo-1-hydroxyanthraquinone, orange needles, m. p. 235°, is produced. 4,4'-Dihydroxydi-1-anthraquinonyl disulphide, reddish-brown, flat prisms, m. p. above 300° (compare Gattermann, A., 1912, i, 998), is conveniently prepared by the

action of an aqueous solution of sodium disulphide on 1-bromo-4-hydroxyanthraquinone dissolved in alcohol, and is reduced by dextrose to 4-hydroxy-1-thiolanthraquinone, red needles, m. p. 194° (methyl thio-ether, shining, red leaflets, m. p. 217°, whereas Gattermann (*loc. cit.*) records 194°; sulphoxide of methyl thio-ether, orange-reddish leaflets, m. p. 226°). Di-4-hydroxy-1-anthraquinonyl monosulphide crystallises in red, intertwined needles, m. p. above 300°, whilst the corresponding sulphoxide forms slender, yellow needles, m. p. 287°. Di-4-hydroxy-1-anthraquinonyl disulphide is oxidised by hydrogen peroxide in sulphuric acid solution to 4-hydroxyanthraquinone-1-sulphonic acid, yellowish-brown needles, m. p. 220° (the sodium and ammonium salts are sparingly soluble in cold water and crystallise in reddish-brown leaflets with metallic glance), and by nitric acid to 3-nitro-4-hydroxyanthraquinone-1-sulphonic acid, yellow, rhombic prisms, m. p. 278°, after darkening above 255° (the sodium, ammonium, and potassium salts dissolve sparingly in cold water and form shining, yellow leaflets). 4-Hydroxyanthraquinone-1-sulphonyl chloride, golden-yellow leaflets, m. p. 246°, is obtained in place of the expected chlorothiol when a suspension of the disulphide in chloroform or glacial acetic acid is treated with chlorine; the corresponding anilide forms shining, yellow needles, m. p. 199°.

1-Bromo-4-methoxyanthraquinone, pale yellow needles, m. p. 195°, is obtained by methylation of the hydroxy-compound with methyl sulphate, and is converted by sodium disulphide into di-4-methoxy-1-anthraquinonyl disulphide, yellow needles, m. p. 265° (compare Gattermann, *loc. cit.*); the latter is not attacked by bromine, and is transformed by chlorine into a sulphonic chloride, which was not further investigated; 4-methoxy-1-anthraquinonyl methyl sulphide, orange-red needles, m. p. 187°, is prepared by reduction of the disulphide, followed by methylation of the thiol so produced.

Di-4-amino-1-anthraquinonyl disulphide, m. p. above 300° (compare Gattermann, *loc. cit.*), is conveniently prepared from 4-chloro-1-aminoanthraquinone and sodium disulphide, and is readily reduced to the corresponding thiol, which could not be isolated owing to its unusual susceptibility to oxidation. It is transformed by chlorine into 3-chloro-4-aminoanthraquinone-1-sulphonyl chloride, orange-red needles, m. p. 230°, when rapidly heated after darkening above 200°; the corresponding acid form slender, orange-yellow needles, m. p. (anhydrous) 217° (decomp. (the ammonium salt forms red needles, m. p. about 304° whilst the anilide, coarse, brownish-red crystals, has m. p. 210°). The sulphonic group is displaced by bromine with formation of 3-chloro-1-bromo-4-aminoanthraquinone, m. p. 217°. 4-Amino-1-chlorothiolanthraquinone is obtained in an impure condition by the action of bromine on aminoanthraquinonyl disulphide, or, preferably, by the reduction of aminoanthraquinonesulphonic acid by hydrobromic and acetic acids; it is thus obtained as an unstable hydrobromide, orange-yellow needles, which decompose

above  $200^{\circ}$ ; mineral acid is removed by contact with alcohol or aqueous acetic acid, but the free amino-compound is too unstable to be isolated. The nature of the hydrobromide is established by the formation from it of the *sulphonanilide*, coarse, reddish-violet needles, m. p.  $180^{\circ}$  (decomp.), and of *4-amino-1-anthraquinonyl resorceryl sulphide*, brownish-violet leaflets, m. p.  $247^{\circ}$ . *Potassium 4-aminoanthraquinone-1-sulphenate*, dark green needles with metallic glance, is prepared from the bromothiol, but attempts to isolate the pure sulphenic acid failed; the constitution of the salt, however, is established by its conversion into *4-aminoanthraquinonyl methyl sulphoxide*, slender, red needles, m. p.  $234^{\circ}$ , which is reduced by hydrobromic and glacial acetic acids to *4-aminoanthraquinonyl methyl sulphide*, m. p.  $210^{\circ}$  (compare Gattermann, *loc. cit.*), and by its oxidation to *4-aminoanthraquinonesulphinic acid*, red needles, m. p.  $191^{\circ}$  (decomp.), which forms a sparingly soluble *potassium salt*.  
H. W.

#### Certain Metallic Derivatives of Hydroxyanthraquinones.

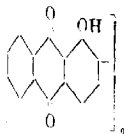
M. L. CROSSLEY (*J. Amer. Chem. Soc.*, 1919, **41**, 2081—2083).—Hydroxyanthraquinones, such as alizarin, anthrapurpurin, and flavopurpurin, form copper, cadmium, nickel, and iron salts when boiled in an organic solvent with the corresponding metallic chlorides, anhydrous sodium acetate, and nitrobenzene. *Copper, cadmium, nickel, iron, cobalt, and chromium* salts of alizarin have been prepared, having the general formula  $C_{14}H_6O_4M$ , except in the case of the cobalt salt, which has  $C_{14}H_6O_5Co$ .

The *copper* and *nickel* salts of anthrapurpurin and flavopurpurin were also prepared. These alizarin salts dye wool a pale shade of the colour which alizarin gives on wool previously mordanted with the corresponding metallic salt.  
W. G.

#### Oxidative Formation of Hydroxydianthraquinonyls from Hydroxyanthraquinones. II. Experiments with Erythrohydroxyanthraquinone and Quinizarin.

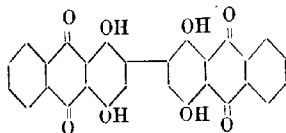
R. SCHOLL, E. SCHEWINGER, and O. DISCHENDORFER (*Ber.*, 1919, **52**, [B], 2254—2261).—The formation of tetrahydroxydianthraquinonyl by the action of hypochlorite on an alkaline solution of alizarin (this vol. i. 64) does not appear to be an example of a general reaction. Further examples, however, are indicated in the patent literature in the cases of erythrohydroxyanthraquinone and quinizarin.

According to D.R.-P. 167461, erythrohydroxyanthraquinone, when melted with potassium hydroxide, yields the hydro-compound of a substance,  $C_{28}H_{14}O_6$ , of unexplained constitution: this is now shown to be 1:1'-dihydroxy-2:2'-dianthraquinonyl (annexed formula), since when distilled with zinc dust in a hydrogen vacuum it gives 2:2'-dianthryl and when heated in carbon dioxide at  $500^{\circ}$  it gives 2:2'-dianthraquinonylene-1:1'-oxide, greenish-yellow needles. The product appears to be



formed by the action of air on the aqueous solution of the melted mass, and not during the process of melting.

Quinizarin, according to D.R.-P. 146223, is converted by salts of weak acids into two compounds,  $C_{28}H_{14}O_8$  and  $C_{28}H_{12}O_8$ , the first of which is described as giving a soluble blue sodium salt, whilst the latter yields a bluish-violet, insoluble sodium salt. It is now shown that only the acid which forms an insoluble sodium salt is a new substance, and that it has the composition  $C_{28}H_{14}O_8$ , whilst the other product is a mixture of this acid with quinizarin. The substance is now shown to be 1:4:1':4'-*tetrahydroxy-2:2'-dianthraquinonyl* (annexed formula), since it gives 2:2'-dianthryl when distilled with zinc dust and a furan derivative when melted with zinc chloride.



A. G. Perkin and W. H. Perkin (T., 1888, **53**, 831) have described the isolation of three substances,  $C_{28}H_{14}O_8$ ,  $C_{28}H_{14}O_7$ , and  $C_{14}H_6O_4$ , by the distillation of sodium anthraquinone-2-sulphonate; the first of these has been submitted to distillation with zinc dust, whereby anthracene and 2:2'-dianthryl are obtained, but the result does not throw any definite light on the constitution of the substance. H. W.

### Isomeric Carvomenthols and Scission of Inactive Carvomenthol into the Optical Antipodes. I. and II.

VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 82—85, 134—137).—The author prepares pure, inactive carvomenthol by reducing carvone by means of zinc dust and sodium hydroxide, transforming the dihydrocarvone thus obtained into the isomeric carvenone by heating it with dilute sulphuric acid, and reducing the carvenone by means of sodium and alcohol. From this inactive carvomenthol, the *levo*-isomeride may be isolated by crystallisation of the less soluble of the two carvomenthol strychnine phthalates, and conversion of this into *l*-carvomenthol hydrogen phthalate, and the latter into *l*-carvomenthol. The carvomenthol hydrogen phthalate prepared from the mother liquors of the above strychnine salt is syrupy, but, when treated with the calculated proportion of ammonia and with silver nitrate, it yields insoluble silver *d*-carvomenthol phthalate, and from this, by way of sodium *d*-carvomenthol phthalate and *d*-carvomenthol hydrogen phthalate, *d*-carvomenthol may be isolated.

#### 1-Carvomenthol strychnine phthalate,

$C_{10}H_{19} \cdot CO_2 \cdot C_6H_4 \cdot CO_2 \cdot C_{21}H_{33}O_2N$ ,  
forms colourless needles, m. p. 155—156°,  $[\alpha]_D -14.76^\circ$  (in alcohol).

1-Carvomenthol hydrogen phthalate,  $CO_2H \cdot C_6H_4 \cdot CO_2 \cdot C_{10}H_{19}$ ,  
forms crystals, m. p. 125°,  $[\alpha]_D -3.80^\circ$  (in alcohol).

1-Carvomerthol,  $C_{10}H_{19} \cdot OH$ , forms an oily, limpid liquid with a faint odour of peppermint, b. p. 218° (corr.),  $D_{15}^{20} 0.9082$ ,  $n_D^{20} 1.461$ ,  $[\alpha]_D -1.82^\circ$ .

Silver *d*-carvomenthol phthalate is obtained as a voluminous, white precipitate, and may be purified by crystallisation from absolute alcohol or by precipitation from chloroform solution by addition of alcohol and ether.

*d*-Carvomenthol hydrogen phthalate forms slender, colourless, needles, m. p.  $109^{\circ}$ ,  $[\alpha]_D + 4.62^{\circ}$  (in alcohol).

*d*-Carvomenthol has b. p.  $218^{\circ}$  (corr.),  $D^{15}_4$  0.9074,  $n^{15}_D$  1.463,  $[\alpha]_D + 1.83^{\circ}$ .

T. H. P.

**Reduction Products of Pulegone: Pulegol. I. and II.**  
 J. PAOLINI (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 190—192, 236—239).—Pulegol (compare Tiemann and Schmidt, A., 1897, 198), which previously has not been obtained free from menthol, has been prepared pure by the author.

The products formed by reducing pulegone by means of sodium and alcohol contain about 30% of a yellow resin,  $C_{20}H_{34}O_2$ , which appears to be identical with the bispulegone obtained by reducing pulegone with aluminium amalgam (compare Harries and Roeder, A., 1900, i, 183), and is of unknown constitution, although it is evidently a mixture of optical isomerides, possibly of ketonic (pinacene) character.

The mixture of alcoholic compounds separated from the reduction products of pulegone by distillation in a current of steam was esterified in the cold with phthalic anhydride (compare A., 1911, 730), the various hydrogen phthalates thus formed being separated by crystallisation and converted into the corresponding alcohols. In this way, *l*-menthol of peppermint oil, a solid *l*-menthol, and *l*-pulegol were isolated.

*l*-Menthol hydrogen phthalate,  $CO_2H \cdot C_6H_4 \cdot CO_2 \cdot C_{10}H_{19}$ , forms tufts of soft, white needles, m. p.  $107$ — $108^{\circ}$ ,  $[\alpha]_D - 107.5^{\circ}$ . The corresponding *l*-menthol is a crystalline solid, m. p.  $44^{\circ}$ , b. p.  $214^{\circ}$  (corr.),  $[\alpha]_D - 49.7^{\circ}$ . *l*-Menthol strychnine phthalate,

$CO_2H \cdot C_6H_4 \cdot CO_2 \cdot C_{10}H_{19} \cdot C_{21}H_{33}O_2N_2$ , forms soft, white needles, m. p.  $157$ — $158^{\circ}$ ,  $[\alpha]_D - 44.46^{\circ}$ .

*d*-Menthol strychnine hydrogen phthalate forms crystals, m. p.  $207$ — $208^{\circ}$ ,  $[\alpha]_D - 11.7^{\circ}$ . *d*-Menthol hydrogen phthalate forms crystals, m. p.  $107$ — $108^{\circ}$ ,  $[\alpha]_D + 18.4^{\circ}$ . *d*-Menthol,  $C_{10}H_{20}O$ , is a solid and has m. p.  $88$ — $89^{\circ}$ , b. p.  $214^{\circ}$ , and  $[\alpha]_D + 21.8^{\circ}$ ; it is a saturated compound, and is possibly identical with the  $\alpha$ -pulegomenthol obtained by Haller and Martine (A., 1905, i, 533) by reducing pulegone by Sabatier's method.

Pulegol hydrogen phthalate,  $C_{10}H_{18}O$ , crystallises in slender, white needles, m. p.  $212^{\circ}$ ,  $[\alpha]_D - 86.8^{\circ}$ . *l*-Pulegol forms slender, white needles with a faint odour of menthol, m. p.  $46$ — $47^{\circ}$ ,  $[\alpha]_D - 54.6^{\circ}$ ; it is an unsaturated compound, and readily decolorises permanganate and bromine solution, the bromide,  $C_{10}H_{18}OBr_2$ , being a dense, colourless, oily liquid.

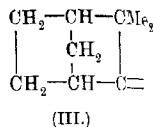
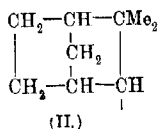
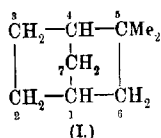
T. H. P.

**Transpositions in the Camphene Series.** G. LANGLOIS (*Ann. Chim.*, 1919, [ix], **12**, 193—264).—In the first part of the



paper, a brief résumé is given of the chemistry of camphene and its derivatives. A closer study has been made of halogenation in this series, and the constitution of the monochloro- and monobromo-derivatives of camphene has been established, and a new method of synthesis for the introduction of carbon containing substituents into the side-chain has been found.

A general outline of the work is given, and the experimental work is to be published later. A new method of nomenclature is advocated for the camphene series based on the hypothetical camphenylene (formula I) and the hypothetical radicles camphenylene (formula II) and camphenylidene (formula III).

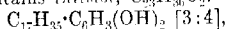


In this system, camphene becomes camphenylidene-6-methane.

W. G.

### Chemical Investigation of Various Natural Lacquers.

RIKO MAJIMA (*J. Tokyo Chem. Soc.*, 1919, **40**, 91—126. Compare A., 1908, i, 437; 1909, i, 402, 945; 1912, i, 883).—Chinese lacquer (from *Rhus vernicifera*, De.) is essentially the same as Japanese lacquer; both contain urushiol. Yunnan lacquer (from *R. succedanea*, L. fil.), Formosan lacquer (from *Semecarpus vernicifera*), and Ivory lacquer (from *R. toricodendron* ?) contain laccol,  $\text{C}_{25}\text{H}_{36}\text{O}_2$ , a homologue of urushiol. Hydrolaccol,  $\text{C}_{17}\text{H}_{25}\cdot\text{C}_6\text{H}_8(\text{OH})_2$  [2:3], m. p. 63—64°, forms a dimethyl ether, m. p. 43—44°, a mononitro-derivative, m. p. 75—76°, and dinitro-derivative, m. p. 86—87°. Burmese lacquer contains thitsiol,  $\text{C}_{23}\text{H}_{30}\text{O}_2$ . Hydrothitsiol,



m. p. 94—96°, forms a dimethyl ether, m. p. 56—57°, and mononitro-derivative, m. p. 75—76°; the dinitro-derivative is difficult to prepare. Hydrothitsiol is therefore very similar to isohydro-urushiol, and probably belongs to the same group. Unlike urushiol and laccol, thitsiol contains a group which is hydrogenated or ozonised only with difficulty.

Siam lacquer is probably a mixture of Yunnan and Burmese lacquers. Korean lacquer is assumed to be identical with Japanese lacquer.

CHEMICAL ABSTRACTS.

**Bromination and Constitution of Caoutchouc.** W. C. SCHMITZ (*Gummi Zeit.*, 1919, **34**, 167—169, 193—195).—Purified rubber which has been "depolymerised" by heating with xylene under a pressure of 15 atmospheres forms an additive compound,  $\text{C}_{20}\text{H}_{32}\text{Br}_{10}$ , when brominated in carbon tetrachloride; this product gradually eliminates hydrogen bromide, with formation of a micro-crystalline compound,  $\text{C}_{20}\text{H}_{30}\text{Br}_8$ , which is insoluble in carbon tetra-

chloride and is quite distinct from the ordinary "caoutchouc tetrabromide." The decabromide is probably an open-chain compound, and it is uncertain whether the disruption of the cyclic caoutchouc molecule occurs during bromination or in the previous depolymerisation. In the bromination of solutions of ordinary rubber, the chemical process is complicated by colloidal phenomena which are absent in the case of the depolymerised hydrocarbon. [See also *J. Soc. Chem. Ind.*, 1920, 73a.] D. F. T.

**Preparation of Double Compounds of Caffeine with Alkali Salts of Acetylsalicylic [*o*-Acetoxybenzoic] Acid.**

CHEMISCHE FABRIK J. A. WÜLFING (Brit. Pat. 136187).—*o*-Acetoxybenzoic acid (2 mols.), an alkali carbonate (1 mol.), and caffeine (1 mol.) are homogeneously mixed, and the mixture is moistened with an alcohol, ester, ketone, or chlorinated hydrocarbon of the aliphatic series to the consistency of a viscous paste, which is kneaded until a sample dissolves in water to a clear solution without the liberation of carbon dioxide. The solvent is then removed by evaporation at a low temperature, and the product, consisting of the *o*-acetoxybenzoate of caffeine and the alkali metal, is finally dried in a vacuum. G. F. M.

**Syntheses in the Cinchona Series. II. Quaternary Salts.**

WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 2090—2120).—The authors have prepared a number of quaternary salts from the different cinchona alkaloids with a view to a study of their bactericidal or, more specifically, pneumococidal powers. The methochlorides, the benzyl chlorides, and the salts formed with the chloroacetyl derivatives of ammonia, the lower aliphatic amines, and benzylamine have been prepared. In the case of the chloroacetyl derivatives of the aromatic amines, the new series of salts with the alkaloids were only sparingly soluble in cold water, the other salts named above being, in general, fairly readily soluble. Solutions of all of the salts, aliphatic or aromatic, gave immediate precipitates with solutions of picric acid or potassium dichromate.

The quaternary salts of the alkaloids with the chloroacetyl derivatives of the aliphatic and aromatic amines were prepared by boiling equimolecular amounts of the components in dry acetone for five to seven hours. The following salts are described.

Cinchonine gives a *methochloride* decomposing at 270°,  $\alpha_D^{20} + 225.1^\circ$ ; a *benzylchloride*, m. p. 280° (decomp.),  $[\alpha]_D^{20} - 164.8^\circ$ ; an *iodoacetamide*, decomposing at about 190°; a *chloroacetamide*, m. p. 110—120° (decomp.),  $[\alpha]_D^{20} + 174.2^\circ$ .

Cinchonidine gives a *methochloride*, m. p. 232—233° (decomp.),  $\alpha_D^{20} - 142.7^\circ$ ; a *chloroacetamide*, m. p. about 190°,  $[\alpha]_D^{20} - 112.5^\circ$ .

Quinine gives a *methochloride*, m. p. 196—198°,  $[\alpha]_D^{20} - 211.7^\circ$ ; a *benzylchloride*, m. p. 183—188°,  $[\alpha]_D^{20} - 230.5^\circ$ ; an *iodoacetamide*, m. p. 175—180°,  $[\alpha]_D^{20} - 152.2^\circ$ ; a *chloroacetamide*, m. p. 190° (decomp.),  $[\alpha]_D^{20} - 159.6^\circ$ ; a *chloroacetanilide*, m. p. 224—225°

g\*

(decomp.),  $[\alpha]_D^{25} = -131.5^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 204—206° (decomp.), and a *nitrate*, m. p. 201—203° (decomp.); *quinine-p-chloroacetylaminophenol*,

$C_{20}H_{24}O_2N_2 \cdot CH_2Cl \cdot CO \cdot NH \cdot C_6H_4 \cdot OH$ ,  
m. p. 205° (decomp.), *quinine-o-chloroacetylaminobenzamide*,  
 $C_{20}H_{24}O_2N_2 \cdot CH_2Cl \cdot CO \cdot NH \cdot C_6H_4 \cdot CO \cdot NH_2$ , m. p. 178—179°  
(decomp.),  $[\alpha]_D^{25} = -164.4^\circ$  (in alcohol).

Quinine gives a *methochloride*, m. p. 250—251° (decomp.),  $[\alpha]_D^{25} + 253.1^\circ$ ; a *benzylochloride*, m. p. 180° (decomp.),  $[\alpha]_D^{25} + 219.9^\circ$ ; an *iodoacetamide*, m. p. 190° (decomp.),  $[\alpha]_D^{25} + 166.2^\circ$  (in alcohol); a *chloroacetamide*, m. p. 205° (decomp.),  $[\alpha]_D^{25} + 207.2^\circ$ ; an *iodoacetylcarbamide*, m. p. 170—175° (decomp.), and a *chloroacetylcarbamide*, m. p. 176—178° (decomp.),  $[\alpha]_D^{25} + 170.9^\circ$ .

Hydroquinine gives a *methiodide*, m. p. 233—235° (decomp.),  $[\alpha]_D^{25} - 107.6^\circ$  (in alcohol); a *methochloride*, m. p. 172—173° (decomp.),  $[\alpha]_D^{25} - 162.9^\circ$ ; a *benzylochloride*, m. p. 202—203.5° (decomp.),  $[\alpha]_D^{25} - 196.9^\circ$ ; an *iodoacetamide*, m. p. 185°;  $[\alpha]_D^{25} - 121.5^\circ$  (in alcohol); a *chloroacetamide*, m. p. 193° (decomp.),  $[\alpha]_D^{25} - 129.1^\circ$ ; a *chloroacetomethylamide*,

$C_{20}H_{26}O_2N_2 \cdot CH_2Cl \cdot CO \cdot NHMe$ ,  
m. p. 160°; a *chloroacetoethylamide*, m. p. 160°; a *chloroacetodiethylamide*; a *chloroacetodiethylamide*, m. p. 209—210° (decomp.),  $[\alpha]_D^{25} - 84.8^\circ$ ; a *chloroacetobenzylamide*,

$C_{20}H_{26}O_2N_2 \cdot CH_2Cl \cdot CO \cdot NH \cdot CH_2Ph$ ,  
m. p. 197—198°,  $[\alpha]_D^{25} - 42.5^\circ$ ; a *chloroacetanilide*, m. p. 210° (decomp.),  $[\alpha]_D^{25} - 95.9^\circ$  (in alcohol), giving a *hydrochloride* and a *dinitrate*; a *m-nitrochloroacetanilide*, m. p. 195—200° (decomp.); a *m-chloroacetylaminacetanilide*, m. p. 150° (decomp.); a *p-chloroacetylaminacetanilide*, m. p. 205°; a *p-chloroacetylaminodimethyl-aniline*,  $C_{20}H_{26}O_2N_2 \cdot CH_2Cl \cdot CO \cdot NH \cdot C_6H_4 \cdot NMe_2$ , m. p. 200° (decomp.),  $[\alpha]_D^{25} - 82.9^\circ$  (in alcohol); a *p-chloroacetylaminodimethyl-aniline*, m. p. 190—195°,  $[\alpha]_D^{25} - 80.5^\circ$  (in alcohol); an *o-chloroacetylaminophenol*, m. p. 185° (decomp.); a *m-chloroacetylaminophenol*, m. p. 205°,  $[\alpha]_D^{25} - 115.7^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 200°; *hydroquinine-p-chloroacetylaminophenol hydrochloride*, m. p. 196—197°; *hydroquinine-4-chloroacetylaminocatechol hydrochloride*,

$C_{20}H_{26}O_2N_2 \cdot CH_2Cl \cdot CO \cdot NH \cdot C_6H_3(OH)_2 \cdot HCl$ ,  
m. p. 196—198° (decomp.); *hydroquininechloroacetyl-o-anisidine*, m. p. 185°,  $[\alpha]_D^{25} - 72.5^\circ$  (in alcohol); *hydroquininechloroacetyl-m-anisidine*, m. p. 190°,  $[\alpha]_D^{25} - 102.9^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 170—171°; *hydroquininechloroacetyl-p-anisidine*, m. p. 190°,  $[\alpha]_D^{25} - 93.9^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 180—184°; *hydroquininechloroacetyl-o-phenetidine*, m. p. 170—172°; *hydroquininechloroacetyl-m-phenetidine hydrochloride*, m. p. 173—174°; *hydroquininechloroacetyl-p-phenetidine*, m. p. 210°,  $[\alpha]_D^{25} - 89.1^\circ$  (in alcohol); *hydroquinine-4-chloroacetylaminoguaiacol*,  $C_{20}H_{26}O_2N_2 \cdot C_6H_3(OH)(OMe) \cdot NH \cdot CO \cdot CH_2Cl$ , m. p. 215° (decomp.); *hydroquinine-3:4-methylenedioxychloroacetanilide*,

$C_{20}H_{26}O_2N_2 \cdot CH_2O_2 \cdot C_6H_3 \cdot NH \cdot CO \cdot CH_2Cl$ ,

m. p. 185°; *hydroquinine-3:4-dimethoxychloroacetanilide*, m. p. 205—210° (decomp.); *hydroquinine-m-chloroacetylaminobenzene-sulphonamide*,  $C_{20}H_{26}O_2N_2CH_2Cl \cdot CO \cdot NH \cdot C_6H_4 \cdot SO_2 \cdot NH_2$ , m. p. 200—205° (decomp.).

Hydroquinidine gives an *iodoacetamide*; a *chloroacetamide*, m. p. 210° (decomp.),  $[\alpha]_D^{25} + 179.9^\circ$ ; *hydroquinidine-p-chloroacetylaminophenol*, m. p. 285°, giving a *hydrochloride*, m. p. 245—250° (decomp.); *hydroquinidinechloroacetyl-p-anisidine*, m. p. 260—265° (decomp.), giving a *hydrochloride*, m. p. 196—200° (decomp.).

Hydrocupreine gives a *chloroacetanilide hydrochloride*, m. p. 213—214° (decomp.), and a *chloroacetyl-p-anisidine hydrochloride*, m. p. 210° (decomp.).

Ethylhydrocupreine gives a *methochloride*, m. p. 198—199°,  $[\alpha]_D^{25} - 176.7^\circ$ , and *iodoacetamide*, m. p. 185°,  $[\alpha]_D^{25} - 115.4^\circ$  (in alcohol); a *chloroacetamide*, m. p. 195°,  $[\alpha]_D^{25} - 114.8^\circ$ ; a *p-chloroacetylaminophenol*, m. p. 178—182°,  $[\alpha]_D^{25} - 71.8^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 196—197°; *ethylhydrocupreinechloroacetyl-p-anisidine*, m. p. 200°,  $[\alpha]_D^{25} - 69.0^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 204—205° (decomp.); *ethylhydrocupreinechloroacetyl-p-phenetidine*, m. p. 210° (decomp.),  $[\alpha]_D^{25} - 75.25^\circ$  (in alcohol), giving a *hydrochloride*, m. p. 208° (decomp.).

Most of the melting points given above are only approximate, as the substances turn to jellies long before they become fluid.

W. G.

**Synthesis in the Cinchona Series. III. Azo-dyes derived from Hydrocupreine and Hydrocupreidine.** MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1919, 41, 2131—2147).—Both hydrocupreine and hydrocupreidine behave in a normal manner as phenolic compounds, and yield well-defined azo-dyes with diazotised aromatic amines, and the authors assume that position 5 in the quinoline nucleus is the place of entrance of the azo-group (compare Giemsa and Halberkann, A., 1919, i, 342). In general, the benzeneazo- and tolueneazo-dyes, as well as those with *m*-substituents in the benzene ring, dye silk various shades of orange. *o*- and *p*-Alkoxy-groups deepen these colours towards the red, whilst the dyes from the naphthylamines dye silk a deep rose colour. These substances have the property of dyeing unmordanted cotton. Many of the substances described below are highly bactericidal *in vitro*. The following azo-dyes have been prepared:

*Benzeneazohydrocupreine*, m. p. 130°, giving a *dihydrochloride*, m. p. 181—183° (decomp.); *o-tolueneazohydrocupreine*, m. p. 110—130° (decomp.); *m-tolueneazohydrocupreine*, m. p. 125—130°, giving a *dihydrochloride*, m. p. 195° (decomp.); *p-tolueneazohydrocupreine*, m. p. 202—205°; *α-naphthaleneazohydrocupreine*, m. p. 146—149° (decomp.); *β-naphthaleneazohydrocupreine*, m. p. 240—244° (decomp.); *dibenzene-p-bisazohydrocupreine*, m. p. 204° (decomp.); *m-nitrobenzeneazohydrocupreine*, m. p. 150.5—151.5°; *p-nitrobenzeneazohydrocupreine*, m. p. 220° (decomp.); *m-acetyl-*

aminobenzeneazohydrocupreine, m. p. 155—180°; *m*-carbamido-benzeneazohydrocupreine, m. p. 165—185° (decomp.); *p*-amino-benzeneazohydrocupreine, m. p. 155—165°; *p*-acetylaminobenzeneazohydrocupreine, m. p. 158—162° (decomp.); *p*-carbamidobenzeneazohydrocupreine, decomposing at 190°; *p*-hydroxybenzeneazohydrocupreine, m. p. 150—160° (decomp.); *p*-benzoyloxybenzeneazohydrocupreine dihydrochloride, m. p. 185—195° (decomp.); 2-methoxybenzeneazohydrocupreine, m. p. 120°; 3-methoxybenzeneazohydrocupreine, m. p. 188—190°; 4-methoxybenzeneazohydrocupreine, m. p. 213—215° (decomp.); 2-ethoxybenzeneazohydrocupreine, m. p. 135—140°; 3-ethoxybenzeneazohydrocupreine, m. p. 90—125°; 4-ethoxybenzeneazohydrocupreine, m. p. 156—161°; 3:4-methylenedioxybenzeneazohydrocupreine, m. p. 177—184°; 3:4-dimethoxybenzeneazohydrocupreine, m. p. 110°; 3-methoxy-4-ethoxybenzeneazohydrocupreine, m. p. 100—135°; 4-methoxy-5-ethoxybenzeneazohydrocupreine, m. p. 75—120°; 3:4-dimethoxy-6-carborybenzeneazohydrocupreine, m. p. 236° (decomp.); *o*-phenylglycolic acid-*p*-azohydrocupreine,

$\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_{19}\text{H}_{33}\text{O}_2\text{N}_2$ ,  
m. p. 199—200° (decomp.); *m*-carborylamidobenzeneazohydrocupreine, m. p. 195° (decomp.), gives a dihydrochloride; *p*-sulphobenzeneazohydrocupreine, m. p. 252° (decomp.) (compare Giemsa and Halberkann, *loc. cit.*), gives a scarlet sodium salt; *m*-sulphonamidobenzeneazohydrocupreine, m. p. 170—190°; *p*-sulphonamidobenzeneazohydrocupreine, m. p. 155—190°; quinolyl-6-azohydrocupreine, m. p. 232—234°; benzeneazohydrocupreidine, m. p. 183—185°, gives a dihydrochloride, m. p. 220—221° (decomp.);  $\alpha$ -naphthaleneazohydrocupreidine, m. p. 132—140°; *p*-nitrobenzeneazohydrocupreidine, m. p. 135—139°; *p*-sulphobenzeneazohydrocupreidine, m. p. 247° (decomp.); benzeneazo-6-hydroxyquinoline has m. p. 160—161·5°. Most of these compounds show considerable softening or sintering and darkening previous to melting. W. G.

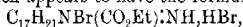
**Final Report on the Alkaloids of Gelsemium.** L. E. SATRE (*J. Amer. Pharm. Assoc.*, 1919, **8**, 708—711).—The investigation was made on about 11·5 kilos. of the drug in N° 20 powder. The following alkaloids isolated as salts were obtained: sempervirine nitrate (about 3 grams), gelsemine hydrochloride (about 8 grams), gelsemidine hydrochloride (1·75 grams), and an amorphous alkaloidal chloride, which is named gelsemoidine hydrochloride. All of these are toxic.

CHEMICAL ABSTRACTS.

**Ethylmorphine Sulphate.** JAMES LESLIE THOMSON (*Pharm. J.*, 1920, [iv], **50**, 7).—Ethylmorphine sulphate has m. p. 207°, and crystallises with 5H<sub>2</sub>O; at 15·5° it dissolves in 9·5 parts of water and in 111 parts of 90% alcohol. W. P. S.

**Strychnine and Brucine.** VI. R. CIUSA (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 185—187).—The action of bromine on isostrychnine in acetic acid solution and subsequent decomposition of the perbromide yields derivatives of the tribromo-base.

$C_{21}H_{21}ON_2Br_3$ , in which two bromine atoms are added at a double linking as in strychnine, while the third replaces a hydroxyl group (A., 1915, i, 893). This conclusion is confirmed by the behaviour of *isostrychnine* towards (1) alcoholic hydrogen bromide in the hot, and (2) benzoyl chloride. The first of these reactions yields a crystalline compound which appears to have the formula



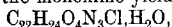
and is to be considered later.

The action of benzoyl chloride on *isostrychnine* suspended in 10% potassium hydroxide solution yields only a small proportion of a compound, m. p.  $174^\circ$ . In pyridine solution, however, the benzoylation gives *benzoylisostrychnine*,  $C_{21}H_{21}O_2N_2Bz$ , which crystallises in colourless needles, m. p.  $174^\circ$ , and has the normal molecular weight in benzene solution. The benzoylation yields also the *benzoate* of the benzoyl derivative,  $C_{21}H_{21}O_2N_2Bz \cdot BzOH \cdot H_2O$ , which forms white needles, m. p.  $127^\circ$ . The *hydrochloride*,  $C_{21}H_{21}O_2N_2Bz \cdot HCl$ , small, colourless needles, m. p.  $219^\circ$ ; the *aurichloride*, yellow needles, m. p.  $195^\circ$ ; and the *dichromate*,  $(C_{21}H_{21}O_2N_2Bz)_2 \cdot H_2Cr_2O_7$ , slender, reddish-yellow needles, were prepared and analysed. The sulphate and nitrate crystallise well, and are slightly soluble in water.

T. H. P.

**Strychnine Alkaloids. XXVII. Conversion of the Methylammonium Salts from Brucine and *apo*Methylbrucine into Quinones.** HERMANN LEUCHS and WALTER HINTZE (*Ber.*, 1919, 52, [B], 2195—2204).—The salt of the quaternary ammonium base which is readily formed by the action of methyl sulphate on brucine shows, like the alkaloid itself, the red coloration with nitric acid, which is due to the formation of quinone; the latter, however, could not be isolated in the pure state or as a salt, and was therefore immediately reduced to the corresponding quinol, which separated from solution as a mixture of *bisapomethylbrucine methanilate*,  $C_{21}H_{23}O_4N_3 \cdot MeNO_3 \cdot H_2O$ , colourless, shining prisms, and *acid sulphate*,  $C_{21}H_{23}O_4N_3 \cdot Me \cdot SO_3H$ , colourless, three-sided plates, in which the additional molecule of water appears to be chemically united, since it is not evolved in a vacuum at  $140^\circ$ . For purification the mixture of salts was transformed by 12*N*-hydrochloric acid into *bisapomethylbrucine methochloride*, leaflets or prisms ( $+H_2O$ ), prisms ( $+2H_2O$ ),  $[a]_D^{25} + 6.54^\circ$  for the monohydrated salt in aqueous solution. Oxidation of the quinol to quinone is conveniently effected with a solution of chromic acid in hydrochloric acid, whereby the substance,  $C_{21}H_{20}O_4N_3 \cdot MeCl \cdot H_2CrO_4$ , bright red leaflets, is obtained, which is analogous to the compound derived from *bisapomethylbrucine* itself (A., 1911, i, 746). A similar oxidation is effected by heating the quinol with a solution of hydroxylamine in hydrochloric acid, when the *monoxime* of the quinone, yellow needles, is produced; this, however, has not the simplest formula,  $C_{22}H_{24}O_4N_3Cl$ , but contains an additional molecule of hydrogen chloride and, according to conditions, either  $4H_2O$ , which may be replaced in part by hydrogen chloride, or  $2H_2O$ . Concentrated nitric acid converts the chloride into the *nitrate*,

$C_{22}H_{24}O_4N_8(NO_3), HNO_3, 2H_2O$ , yellow prisms, which is hydrolysed by water to the substance,  $C_{22}H_{24}O_4N_8(NO_3), H_2O + H_2O$ , red prisms, which is re-converted by acid into the yellow nitrate. Similarly, the dichloride of the monoxime yields a hydrate,



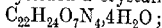
slender, red needles, when the excess of hydrochloric acid is removed preferably by addition of alkali hydroxide (1 mol.). By the aid of a second molecule of alkali hydroxide, the residual chlorine atom can be removed as hydrogen chloride, and a betaine-like compound,  $C_{22}H_{25}O_5N_3$ , orange-red prisms, is produced.

The yellow nitrate of the oxime is only formed with gently warmed nitric acid. At a higher temperature a more complex action occurs in which nitration is accompanied by oxidation of the quinone-oxime or nitrosophenol group to the nitrophenol group and a molecule of water is added; the nitrate,  $C_{22}H_{25}O_{11}N_5$ , which is thus produced, is identical with the product of the oxidation of the oxime of methylcacotheline (following abstract), from which it is more readily produced.

In a similar manner, bisapomethylbrucine methochloride is converted through the quinone by 5*N*-nitric acid at 50–60° into methylcacotheline methonitrate. On the other hand, only quinone formation, unaccompanied by nitration, is observed with concentrated nitric acid at 0°, so that in this instance, in contrast to that of bisapomethylbrucine itself (A., 1911, i, 746), it was not possible to obtain a nitrated but not hydrated quinone. H. W.

**Strychnine Alkaloids. XXVIII. Transformations and the Violet Colour Reaction of Methylcacotheline.** HERMANN LEUCHS and WALTER HINTZE (*Ber.*, 1919, 52, [B], 2204–2224. Compare A., 1919, i, 35).—Previous investigation of the methonitrate of the cacotheline bases (now termed methylcacotheline) had established the probability that it, in accordance with its mode of formation from brucine dimethosulphate, is a nitrated and hydrated quinone, but the function of the added water was left unexplained. Further evidence of its quinonoid nature is now adduced by the isolation of a semicarbazone as nitrate,  $C_{23}H_{27}O_7N_6 \cdot NO_3 \cdot 3H_2O$ , the semicarbazone of the methochloride, slender, pale yellow needles, and the monophenylhydrazone as nitrate,  $C_{23}H_{29}O_6N_5 \cdot NO_3 \cdot 3H_2O$ , brownish-red, oblique prisms. To determine whether water has been added in such a manner that the acid amide group  $\cdot CO \cdot N \cdot$  of brucine has been converted into  $\cdot CO_2H | H \cdot N <$ , attempts have been made to identify the presence of the carboxyl group in two ways. On the one hand, hydrogen chloride has been removed from the semicarbazone hydrochloride by the agency of silver oxide (or, in general, a molecule of acid from the salts by a molecule of alkali), whereby a crystalline betaine,  $C_{28}H_{36}O_7N_6$ , has been produced which readily re-forms the original salts with acids. On the other hand, the presence of the carboxyl group is shown by the conversion of the semicarbazone nitrate into its methyl ester,  $C_{24}H_{29}O_7N_6Cl$ . The phenylhydrazone only yielded an amorphous betaine, but methylcacotheline itself gave a crystalline betaine,  $C_{22}H_{23}O_7N_3$ , and, as no

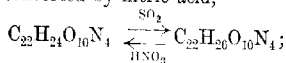
other acidic group can be present, may thus be regarded as containing the carboxyl group. The chloride of the monoxime described previously (*loc. cit.*) also yielded a crystalline *betaine*,



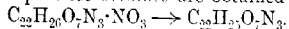
possibly, in this instance, the oxime or the tautomeric nitroso-phenol group could take part in the dehydration, but this view is rendered improbable by the isolation of a crystalline *monomethyl* and *monoethyl* ester.

The *nitrate* of the monoxime can only be obtained from the chloride by the use of metallic nitrates, since the oxime is oxidised when warmed with even *N*-nitric acid, the quinoneoxime or nitroso-phenol group being converted into the nitrophenol group, a second nitro-group being thus introduced into the molecule; this '*dinitrophenol*' also yields a crystalline *betaine*,  $\text{C}_{22}\text{H}_{24}\text{O}_8\text{N}_4$ , whilst its salts can be reduced to a '*diaminophenol*,'  $\text{C}_{22}\text{H}_{26}\text{O}_4\text{N}_4\text{Cl}\cdot 2\text{HCl}$  or  $1\text{HCl}$ , which can be obtained less smoothly from the nitroquinonemonoxime. According to these reactions, the formula of methylcatheline may be resolved thus:  $\text{C}_{16}\text{H}_{17}\{-\text{CO}-\text{CO}-; : \text{C}\cdot\text{NO}_2; \text{NMeNO}_2; =\text{NH}; \cdot\text{CO}_2\text{H}; =\text{CH}(\text{OH})\}$ .

The violet coloration caused by the action of stannous chloride or sulphur dioxide on methylcatheline has been previously investigated and attributed to the conversion of the quinone into the corresponding quinol, the necessary hydrogen being regarded as obtained by the conversion of the secondary alcoholic group of the brucine molecule into the keto-group. Further examination has now been made on the action of methylcatheline and similar salts towards sulphur dioxide in the presence of mineral acids; methylcatheline itself yields a crystalline, dark violet *nitrate*, which, however, contains two hydrogen atoms more than the original salt into which it is re-converted by nitric acid,



the corresponding chloride,  $\text{C}_{22}\text{H}_{24}\text{O}_7\text{N}_3\text{Cl}$ , similarly yields a violet *quinol*,  $\text{C}_{22}\text{H}_{26}\text{O}_7\text{N}_3\text{Cl}$ , from which it is re-formed by ferric chloride. The behaviour of the acid sulphate is precisely similar, the quinol sulphate re-forming the original material on treatment with ferric sulphate. The sulphite thus occupies a peculiar position in that reduction in this case only is caused by hydrogen derived from within the molecule. The presence of acid radicles which are not ionised is not essential to the production of the violet colour, since they can be removed by warming with one (or two) molecules of alkali, whereby deep violet *betaines* are obtained:



With the object of demonstrating the presence of the phenol group in the violet quinols, the violet chloride was boiled with acetic anhydride and sodium acetate; the *product*, however, did not contain the acetyl group, but was formed by loss of a molecule of hydrogen chloride and of water from the original substance. It appears to have a *betaine* structure, since it readily yields additive products with acids, and probably is a phenol *betaine*.



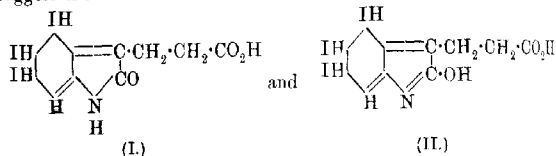
Reduction of the betaine anhydride,  $C_{22}H_{23}O_6N_3$ , with tin and hydrochloric acid yields the aminoquinol,  $C_{22}H_{26}O_4N_3Cl \cdot HCl \cdot 2H_2O$ , previously obtained from methylcatheline and formulated with  $1H_2O$ . A molecule of water appears to be eliminated during the reduction of methylcatheline in a manner similar to that observed during the action of acetic anhydride on the violet quinol. The composition of the amine hydrochloride varies considerably, and the following forms have been prepared and analysed:

$C_{20}H_{26}O_5N_3Cl \cdot HCl$ ,  
needles;  $C_{22}H_{28}O_5N_3Cl \cdot 2H_2O$ , trapezoidal tables;

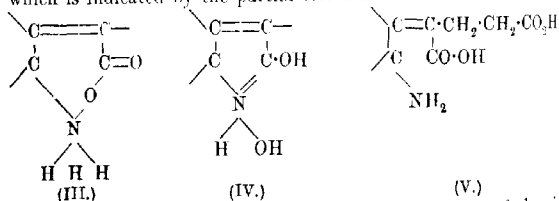
$C_{22}H_{28}O_5N_3Cl \cdot HCl$ ,  
rectangular or quadratic tables; from the first of these, hydrogen chloride is eliminated at  $100^\circ$ , whilst the third is stable at this temperature.

H. W.

**The Chemical Identification of Thyroxin.** II. E. C. KENDALL and A. E. OSTERBERG (*J. Biol. Chem.*, 1919, 40, 265—334).—Thyroxin, the physiologically active constituent of the thyroid gland (A., 1919, i, 497), can exist in two tautomeric forms. The *keto*-form (I), which is by far the more stable, crystallises in long needles, m. p.  $250^\circ$ ; the enol form (II) crystallises in rosettes of needles, m. p.  $204^\circ$ . From a consideration of the chemical behaviour of the substance, so far as it is yet known, the authors suggest the formulæ



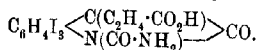
Further, there is evidence that by combination with the elements of a molecule of water, two further forms may exist, melting at  $225^\circ$  (III) and  $216^\circ$  (IV) respectively, the suggested nature of which is indicated by the partial formulæ



Addition of an acid to the enolic form leads to fission of the ring and formation of an amino-acid (V), of which III is an internal salt. For the evidence on which the authors base these formulæ, the original must be consulted.

The *acetyl* derivative crystallises in short, curved needles, m. p.  $228$ — $235^\circ$  (decomp.). The *sulphate* has the formula  $C_{22}H_{22}O_{10}N_2I_2S$ .

The hydrochloride crystallises in star-shaped plates. When treated with cyanic acid, thyroxin yields a *carbamyl* derivative,



Many mono- and di-basic metallic salts of thyroxin have been prepared, but although they are beautifully crystalline, they have not been obtained in a pure condition. A *dimethyl* ester has been prepared, and is hydrolysed to a *monomethyl* ester by alkali hydroxides.

Thyroxin is not easily oxidised or reduced. When exposed to sunlight in weak alkaline solution, it is very unstable. Within twenty-four hours, the solution turns pink or yellow, deepening to a brown, and an aromatic odour is produced. The development of the pink colour is accompanied by the splitting off of iodine in the form of hypoiodous acid.

J. C. D.

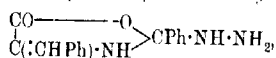
#### Constitution of Arylanthranils, Lactimides, and Lactimones.

GUSTAV HELLER and HILDE LAUTH (*Ber.*, 1919, 52, [B], 2295–2303).—In a previous communication (Heller, A., 1915, i, 844) it has been shown that acylanthranils react with hydrazine hydrate in alcoholic solution to yield 3-hydrazino-3-aryl-3:4-dihydrobenzoxazones, and the reaction is interpreted as in favour

of the formula  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CO} \\ \text{N} \cdot \text{COR} \end{array} \right\rangle$  for the acylanthranils, the behaviour being difficult to reconcile with the alternative formula  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CO} \cdot \text{O} \\ \text{N} = \text{CR} \end{array} \right\rangle$ . A number of somewhat similarly constituted compounds have now been examined.

Anthranoylanthranilic anhydride and acetylanthranoylanthranilic anhydride (Schroeter, A., 1917, i, 529, 620) are converted by hydrazine hydrate in warm alcoholic solution into 3-hydrazino-3-o-aminophenyl-3:4-dihydrobenzoxazone, pale yellow needles, m. p. 200° (decomp.), and 3-hydrazino-3-o-acetylamino-phenyl-3:4-dihydrobenzoxazone, colourless, thread-like crystals, m. p. 216° (decomp.); these substances are decomposed by alkali, and, on acidification with acetic acid, the lactone is re-formed in a somewhat impure condition. It appears, therefore, that complex acylanthranils contain the same ring as is present in the simpler substances.

Benzoylamino-cinnamic lactimide and acetylamino-cinnamic lactimide react similarly with hydrazine hydrate, yielding, respectively, 5-keto-2-hydrazino-2-phenyl-4-benzylidenetetrahydro-oxazole,



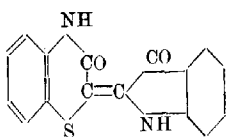
colourless needles, m. p. 153–154° (*benzylidenehydrazino*-derivative, colourless needles, m. p. about 220° after darkening from 145°), and 5-keto-2-hydrazino-2-methyl-4-benzylidenetetrahydro-oxazole, coarse crystals and clusters of needles, m. p. about 180°

(decomp.) after darkening from 160°. For reasons similar to those advanced in the case of the acylanthranils, the original substances

must have the constitution  $\text{CHPh} \cdot \text{C} \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{N} \cdot \text{CO} \cdot \text{R} \end{smallmatrix}$ .

$\alpha$ -Benzoylaminoisobutyric anhydride (Mohr and Geis, A., 1908, i, 339; 1910, i, 117) is transformed by hydrazine hydrate into 5-keto-2-hydrazino-2-phenyl-4:4-dimethyltetrahydro-oxazole, slender needles, m. p. 134°, and must therefore have the lactam formula. The isomeric  $\alpha$ -benzoylaminoisobutyric hydrazide, obtained by the action of hydrazine hydrate on the acid chloride, has m. p. 248° (decomp.). H. W.

**Dyes Derived from Ketodihydro-1:4-benzisothiazine.** W. HERZOG (*Ber.*, 1919, 52, [B], 2270—2274).—Ketodihydrobenzothiazine reacts with  $\alpha$ -isatinanilide in a solvent of high boiling



point, such as ethyl benzoate, to yield 2(2'-indoxyl)-3-ketodihydro-1:4-benzisothiazine (annexed formula), dull, brownish-violet needles with metallic glance, m. p. above 300°, which dyes cotton bluish-violet and wool reddish-violet. 2(2'-Thionaphthen)-3-ketodihydro-1:4-benzisothiazine, yellow, silky needles, m. p. above 300°, prepared similarly from thionaphthen-quinoneanilide, has little affinity for the textile fibres.  $\beta$ -Isatinanilide yields 2(3'-indoxyl)-3-ketodihydro-1:4-benzisothiazine, orange-red, silky needles, m. p. about 270°, which has very little affinity for the textile fibres.

The inferiority of the substances as dyes in comparison with indigo-blue and thioindigo-red is readily interpreted according to the Claus hypothesis, since they contain only one quinonoid indogen, whilst the latter dyes contain two such groups. H. W.

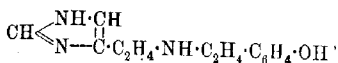
**Certain Arylamino-derivatives of 4(5)-Methyl-5(4)-amino-methylglyoxaline and the Syntheses of 4(5)-( $\beta$ -p-Hydroxyphenyl)ethyl- $\beta$ -aminoethylglyoxaline.** OTTO GERNGROSS (*Ber.*, 1919, 52, [B], 2304—2318).—The anil of 4(5)-methylglyoxaline-5(4)-aldehyde (Gerngross, A., 1912, i, 314) is reduced by sodium in boiling isoamyl-alcoholic solution in an atmosphere of hydrogen to 4(5)-methyl-5(4)-anilinoethylglyoxaline,  $\text{CH} \begin{smallmatrix} \diagup \text{NH} \cdot \text{CMe}_2 \\ \diagdown \text{N} - \text{C} \text{CH}_2 \cdot \text{NHPh} \end{smallmatrix}$

slender needles from water, m. p. 183° (corr.) [hydrochloride, four-sided leaflets, m. p. 201° (corr.) after becoming discoloured at 175° and softening at 195°]; the corresponding benzoyl derivative crystallises in shining, four-sided plates, m. p. 206° (corr.), yields a hydrochloride, m. p. 235° (corr.), and does not couple with diazobenzenesulphonic acid in alkaline solution. The preparation of the aniline derivative is only conveniently effected in this manner when very small quantities of material are required; for larger

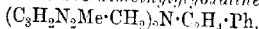
amounts, it is more conveniently produced by the action of aniline (2 mols.) on a solution of methylchloromethylglyoxaline hydrochloride (1 mol.) in methyl alcohol (compare Ewins, T., 1911, **99**, 2034); under these conditions, its formation is accompanied to a greater or less extent by that of *N*-phenyliminobis-4:5-dimethyl-

glyoxaline,  $\text{NPh}(\text{CH}_2\cdot\text{C}\begin{smallmatrix} \text{CM}\cdot\text{NH} \\ \text{N}=\text{CH} \end{smallmatrix})_2$ , small needles, m. p. 199–200° (corr.), from which it can be readily separated by taking advantage of the very sparing solubility of the latter in boiling acetone.

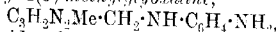
[With HANS NAST.]—The synthesis of 4(5)-(β-*p*-hydroxyphenylethyl-β-aminoethyl)glyoxaline,



is described, which is of pharmacological interest, since it contains the active principles of *Secale cornutum* and tyramine united to one another. 5(4)-β-Phenylethylaminomethyl-4(5)-methylglyoxaline is obtained by slowly adding a solution of the hydrochloride of 4(5)-methyl-5(4)-chloromethylglyoxaline in methyl alcohol to β-phenylethylamine dissolved in slightly methyl-alcoholic water; the crude product is converted successively into the *dipicrate*, prisms, m. p. 211° (corr.) after softening at 204°, and the *dihydrochloride*, shining, hygroscopic, crystalline leaflets, m. p. 254° (corr.; decomp.) [*aurichloride*, yellow crystals, m. p. 215° (corr.)]. Small quantities of β-phenylethyliminobis-4:5-dimethylglyoxaline,



are produced during this reaction, and this substance becomes the main product when care is not taken to maintain a constant excess of the amine; the *tripicrate*, shining, yellow crystals, m. p. 176° (corr.) after softening at 160°, the hygroscopic *hydrochloride*, and the *platinichloride*, which darkens above 200°, but does not melt below 270°, are described. Similarly, the hydrochloride of methylimidazolylmethyl chloride and *p*-phenylenediamine yield 5(4)-*p*-aminoanilinomethyl-4(5)-methylglyoxaline,



the *trihydrochloride*, four-sided, rhombic plates, m. p. 257° (decomp.), and *dipicrate*, large, yellow crystals, m. p. 219–220° (decomp.), of which are described.

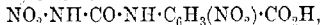
β-Aminoethylglyoxaline condenses with *p*-hydroxyphenylethyl chloride in methyl-alcoholic solution at 100° to yield 4(5)-(β-*p*-hydroxyphenylethyl-β-aminoethyl)glyoxaline; the crude product is treated with hydrochloric acid to remove the excess of the histamine base, and is purified by successive conversion into the *dipicrate*, m. p. 203.5° (corr.; decomp.), the *dihydrochloride*, colourless rods, m. p. 202–203° (corr.), and the free base, microscopic, four-sided prisms, m. p. 157° (corr.); the *mapohydrochloride* forms four-sided platelets, m. p. 195° (corr.).

H. W.

**Quinazolines. XXXIV. The Synthesis of certain Nitro- and Amino-benzoyleneureas [Diketotetrahydroquinazolines] and some Compounds Related Thereto.** MARSTON

TAYLOR BOGERT and GEORGE SCATCHARD (*J. Amer. Chem. Soc.*, 1919, **41**, 2052—2068).—A supplement to, and an elaboration of, work previously published (compare A., 1916, i, 672), certain new compounds being described. Methyl anthranilate, when condensed with potassium isocyanate in acetic acid solution, yielded methyl *o*-carbamidobenzoate, m. p. 177—177.5° (corr.). 6-Nitro-2:4-diketo-1:2:3:4-tetrahydroquinazoline, m. p. 330—331° (corr.), gives a sodium salt, which is colourless at limit 7 on the Sørensen scale, but at 7.5 and on to 11 very slowly develops a greenish-yellow colour. The development of colour is, however, too slow for the salt to be of any use as an indicator. 6:8-Dinitrodiketotetrahydroquinazoline (*loc. cit.*) gives potassium and ammonium salts which resemble the sodium salt in general behaviour, except that the ammonium salt decomposes without explosion. The authors find higher m. p.'s for certain quinazoline derivatives than did Abt (compare A., 1889, 609). Thus 2:4-dichloroquinazoline has m. p. 119.5° (corr.); 2:4-dimethoxyquinazoline has m. p. 74°; 2:4-diketo-1:3-dimethyltetrahydroquinazoline has m. p. 167—168° (corr.).

*o*-Carbamidobenzoic acid when nitrated with nitric acid (D 1:5) at -5° to -10° yielded 5-nitro-2-nitrocarbamidobenzoic acid,



which it was very difficult to purify. Its methyl ester, decomposing at 184—185° (corr.), was obtained by nitration of methyl *o*-carbamidobenzoate. In an endeavour to clear up the chemistry of 5-nitro-2-acetylaminobenzoic acid, the authors have prepared a specimen, m. p. 218° (corr.), and its barium, calcium, ferric, copper, lead, and silver salts. Similarly, they prepared 5-nitro-2-amino-benzoic acid, m. p. 278° (corr.; decomp.), and its sodium, potassium, and ammonium salts. It gives a methyl ester, m. p. 168° (corr.).

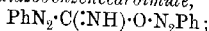
The proof that the compound obtained by Bogert and Geiger (compare A., 1912, i, 395, 510) by the nitration of 4-quinazolone is 6-nitro-4-quinazolone is supplied by the preparation of the same compound by fusing together 5-nitroanthranilic acid and formamide.

W. G.

**New Type of Substances Derived from Diazonium Compounds and Alkali Cyanides.** GUSTAV HELLER and MARIE MEYER

(*Ber.*, 1919, **52**, [B], 2287—2294).—When an aqueous solution of a benzenediazonium salt is added to a solution of potassium cyanide in the presence of an excess of potassium hydroxide, a yellow oil is formed, which immediately yields a colourless solution, from which an unstable, sparingly soluble, red salt gradually separates; this slowly decomposes, even in the cold liquid, with evolution of nitrogen and development of the odour of isocyanide. The corresponding free compound, however, is more stable and has the formula  $\text{C}_{13}\text{H}_7\text{ON}_5$ . The colour of the substance, its failure to yield hydroxylamine when treated with acids, and its reduction by

hydrogen to a colourless derivative lead the authors to consider it to be *benzenediazoxydiazobenzenecarbimide*,

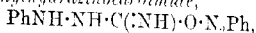


confirmatory evidence is deduced from the fact that it is only formed from *syn*-benzenediazonium hydrate and salt of hydrocyanic acid, and not from the *anti*-diazotate and substances which contain the cyano-group united to carbon or nitrogen.

The *potassium* salt of benzenediazoxydiazobenzenecarbimide forms dark red leaflets, m. p.  $239^\circ$  (decomp.), whilst the *sodium* salt consists of bronze-like leaflets, m. p.  $209^\circ$  (decomp.). The *lead*, *mercurous*, *manganese*, *silver*, *copper*, *cobalt*, *bismuth*, *stannous*, *cadmium*, *zinc*, and *mercuric* salts are described. The corresponding free substance crystallises in red needles, m. p.  $92^\circ$ , with violent evolution of gas. Attempts to obtain a benzoyl or methyl derivative were unsuccessful. *p*-Toluenediazoxydiazobenzenecarbimide, m. p.  $111^\circ$  (decomp.), is converted by phenylcarbimide into *p*-toluenediazoxydiazobenzenecarbimidephenylcarbamide,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\cdot\text{C}(\text{N}\cdot\text{CO}\cdot\text{NHPh})\cdot\text{O}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Me}$ , orange-yellow crystals, m. p.  $148^\circ$  (decomp.). *o*-Toluenediazoxydiazobenzenecarbimide forms bluish-red rods, m. p.  $100^\circ$  (decomp.).

The sodium salt of benzenediazoxydiazobenzenecarbimide slowly decomposes in aqueous solution, yielding nitrogen, aniline, benzonitrile, ammonia, and nitrite, but not phenol. The free substance is decomposed by hot water, yielding smeary products, from which traces of phenol and benzonitrile could be isolated by distillation with steam.

The sodium salt of benzenediazoxydiazobenzenecarbimide is reduced by sodium hyposulphite in alkaline solution, by alkaline stannous chloride, by zinc dust, and acetic or hydrochloric acid in alcoholic solution, or by phenylhydrazine in alcoholic solution to *benzenediazoxyphenylhydrazinocarbimide*,



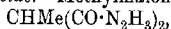
colourless needles or crystalline aggregates, m. p. about  $154^\circ$  (decomp.), which is converted by methyl sulphate into the corresponding *methyl* derivative, m. p.  $137$ – $138^\circ$  (decomp.). Protracted reduction of benzenediazoxydiazobenzenecarbimide by zinc and acid leads to the formation of aniline, whilst, in a similar manner, phenylhydrazine is formed when stannous chloride and hydrochloric acid act on a solution of the substance in glacial acetic acid. Benzenediazoxyphenylhydrazinocarbimide yields practically the same products as does the unreduced compound when it decomposes in cold alkaline solution; in acid solution, it is gradually decomposed, with the formation of phenol. *o*-Toluenediazoxy-*o*-tolylhydrazinocarbimide forms colourless crystals, m. p.  $150^\circ$  (decomp.).

H. W.

**The Special Reactions in the Transformation of the Azides of Carboxylic Acids. I.—VI.** THEODOR CURTIUS (*J. pr. Chem.*, 1916, [ii], **94**, 273–382).—The “normal” reaction of the acid azides, and their formation, are summarised as follows:  $\text{R}\cdot\text{CO}_2\text{Et} \rightarrow \text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2 \rightarrow \text{R}\cdot\text{CO}\cdot\text{N}_3 \rightarrow \text{R}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$  or

$R \cdot NH \cdot CO \cdot NH \cdot R \rightarrow R \cdot NH_2$ , numerous examples of which have already been given in the case of mono-, di-, and even tri-carboxylic acids (most recent notices: A., 1914, i, 873; 1915, i, 124, 169, 787, 872). "Special" reactions are given by (1) the azides of acids having two  $-CO \cdot N_3$  groups attached to the same carbon atom, (2) by hydroxy-acids and their ethers, and (3) by  $\alpha$ -amino- and  $\alpha$ -acylamino-acids. In the first case, the ultimate products are generally the aldehydes or ketones produced by the hydrolysis of the methylenediamines,  $CHR(NH_2)_2$  or  $CRR'(NH_2)_2$ . Examples are now given. The second section is dealt with in Parts VII. to XIII. of this series (A., 1917, i, 635—639), and the third section in Parts XIV. to XVII. (A., 1918, i, 44).

I. [With WILHELM CÄSAR].—*Hydrazide and Azide of Methyl- and isoAmylmalonic Acids*.—Methylmalonodihydrazide,

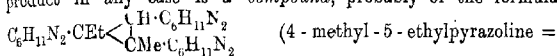


crystallises in silky needles, m. p. 172—173° (compare Bülow and Weidlich, A., 1906, i, 981), forms a *dihydrochloride*, m. p. 168°, a *dibenzylidene* compound, m. p. 251° (*ibid.*), a *disalicylidene* compound, glistening leaflets, m. p. 216—217°, a *diisopropylidene* compound, by boiling with acetone, minute needles, m. p. 158—159°, and a very explosive, yellow *diazide*,  $CHMe(CO \cdot N_3)_2$ . This reacts with aniline to form methylmalondianilide, m. p. 182° (Meyer and Bock, A., 1906, i, 726), and with *p*-toluidine to give the *di-p*-toluidide (Commanducci and Lobello, A., 1905, i, 271). It reacts with alcohol to form an oily urethane, which yields carbon dioxide and acetaldehyde on boiling with dilute sulphuric acid. *isoAmylmalonodihydrazide* forms silky crystals, m. p. 140° (decomp.), and gives a *dihydrochloride*, silky leaflets, a *dibenzylidene* compound, microscopic leaflets, m. p. 240°, and a *disalicylidene* compound, white tablets, m. p. 186—187°. The *diazide* is a pungent-smelling oil which reacts with aniline to give *isoamylmalondianilide*, silky needles, m. p. 185°, and with alcohol to form a urethane, this being hydrolysed by dilute sulphuric acid to *isohexaldehyde*,  $C_5H_{11} \cdot CHO$ . The aqueous distillate of the aldehyde reacts with benzhydrazide to give the *benzhydrazone*,  $C_5H_{11} \cdot CH \cdot N \cdot NHBz$ , silky needles, m. p. 215°. *Dimethylmalonodihydrazide* crystallises in prisms, m. p. 208°, but gives poor results in the subsequent reactions, acetone being recognised, however, as the ultimate product. *Benzylmethylmalonodihydrazide* forms silky leaflets, m. p. 260°.

II. [With HEINRICH RECHNITZ].—*Transformation of Ethylmalondiazide into Propaldehyde, and Transformation of Propaldazine into 4-Methyl-5-ethylpyrazoline*.—Ethylmalonodihydrazide forms slender needles, m. p. 168° (compare Bülow and Bezenhardt, A., 1910, i, 233), and gives a *dihydrochloride*, m. p. 180—181°, a *dipicrate*, yellow needles, m. p. 187° (decomp.), a *dibenzylidene* compound, m. p. 241—242° (decomp.), and a *disalicylidene* compound, m. p. 201°. The *diazide* is very explosive, but may be converted into the dianilide and *di-p*-toluidide, m. p. 288°, or into the diurethane,  $CHEt(NH \cdot CO_2Et)_2$ , which is hydrolysed by dilute sulphuric acid to propaldehyde. The final yield is very poor,

however, as the yield of azide is only 35–40% to begin with. Propaldazine,  $N_3(\text{CHEt})_2$ , is a colourless oil with fishy odour, b. p. 143–145°,  $D_{20}^{25}$  0.844,  $n_D^{25}$  1.379, and it reacts with maleic acid in absolute alcohol to form *hydrazine maleate*,  $N_2H_4C_4H_4O_4$ , very slender needles, m. p. 144° (decomp.), and 4-methyl-5-ethylpyrazoline,  $NH<\begin{smallmatrix} N=CH \\ CHEt \cdot CHMe \end{smallmatrix}$ .

This is a colourless liquid with the odour of peppermint, b. p. 105–107°/18 mm., and is very stable in solution in dilute sulphuric acid. It gives blue and white precipitates with Fehling's solution and mercuric chloride respectively, but does not reduce these agents. With *p*-toluenediazonium sulphate it gives a brick-red compound, which dissolves in concentrated hydrochloric acid with deep bluish-violet colour, the solution becoming pale red on dilution. The yield of the pyrazoline is improved if the alcoholic mixture of propaldazine and maleic acid is heated, or if hydrazine maleate is mixed with propaldehyde, but the chief product in any case is a compound, probably of the formula



$C_6H_{12}N_2$ ). This is a yellowish-red, viscous oil, b. p. 245–250°/18 mm., which turns red litmus blue, but only forms oily salts. It has the reactions of the simple 4-methyl-5-ethylpyrazoline and is apparently formed by the elimination of two molecules of ammonia from four of the pyrazoline. The alkaline liquid left after the extraction of the two bases contains an amount of ammonia which agrees with this view, and fumaric acid is also present.

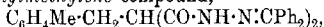
III. [With OWEN E. MOTT, repeated and in part amended by WILHELM SIEBER.]—*Hydrazide and Azide of Benzylmalonic Acid*.—Benzylmalonodihydrazide,  $CH_2Ph \cdot CH(CO \cdot N_3H_3)_2$ , crystallises in slender, glistening needles, m. p. 164°, forms a dihydrochloride, m. p. 135°, and a dibenzylidene compound, small needles, m. p. 220°, and changes into secondary benzylmalonohydrazide,  $CH_2Ph \cdot CH < \begin{smallmatrix} CO \cdot NH \\ CO \cdot NH \end{smallmatrix}$ , glistening leaflets, m. p. 241°, when

(a) its hydrochloride is kept in the moist condition or heated for some hours at 100°, (b) it is treated with alcoholic iodine, or (c) it is treated with sodium nitrite in the presence of a slight excess of hydrochloric acid. In the last reaction benzylmalonyldiazide, an explosive, yellow oil, is the chief product, and the by-product can be suppressed if an excess of acid is used. The diazide may be converted into the dianilide,  $CH_2Ph \cdot CH(CO \cdot NHPh)_2$ , m. p. 217°, and diurethane,  $CH_2Ph \cdot CH(NH \cdot CO_2Et)_2$ , a mass of very slender needles, m. p. 166°, the latter being hydrolysed by 2% sulphuric acid to phenylacetaldehyde, b. p. 81–82°/12 mm., which forms a benzhydrazone,  $CH_2Ph \cdot CH \cdot N \cdot NHbz$ , needles, m. p. 148–149°, and a *m*-nitrobenzhydrazone, m. p. 152°.

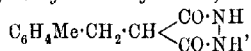
IV. [With CARLO MARANGOLO.]—*Hydrazide and Azide of m-Xylylmalonic Acid* (*m*-Methylbenzylmalonic Acid).—*m*-Xylylmalonodihydrazide [*m*-methylbenzylmalonodihydrazide],  $C_6H_4Me \cdot CH_2 \cdot CH(CO \cdot N_3H_3)_2$ ,



crystallises in silky needles, forms a hygroscopic *dihydrochloride*, m. p. 135—136° (decomp.), a *dibenzylidene* compound, small, glis-  
tening needles, m. p. 219°, a *disalicylidene* compound, m. p. 185—186°, a *disopropylidene* compound, m. p. 182° (from acetone),  
and a *bisdiphenylmethylen*e compound,

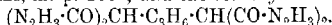


m. p. 164° (from benzophenone). The dihydrazide changes into the  
*secondary m-methylbenzylmalonohydrazide*,



m. p. 236—237°, when treated with alcoholic iodine. The unstable  
*diazide* may be converted into the dianilide, m. p. 193°, *di-p-tolu-*  
*ridide*,  $\text{C}_6\text{H}_3\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$ , slender needles, m. p.  
190°, and crude *diurethane*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}\cdot\text{CO}_2\text{Et})_2$ , which is  
hydrolysed by dilute sulphuric acid to *m-tolylacetaldehyde*,  
 $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CHO}$ . This is a pleasant-smelling, pale yellow, refrac-  
tive oil, b. p. 99—100°/18 mm., which forms an oily *phenylhydra-*  
*zone*, a *benzhydrazone*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{N}\cdot\text{NHBz}$ , long needles,  
m. p. 129—130°, and a *m-nitrobenzhydrazone*, very pale yellow,  
prismatic needles, m. p. 115—116°.

V. [With GOTTFRIED GRANDEL.]—*Hydrazide and Azide of Pen-*  
*tane-ααα-tetracarboxylic Acid and of cyclobutane-1:1-dicarboxylic*  
*Acid*.—The ethyl esters of these acids are obtained by adding a  
mixture of trimethylene bromide and ethyl malonate to a mass of  
sodium ethoxide in alcohol. If the mixture is added rapidly and  
the temperature is only controlled sufficiently to prevent undue  
violence, the yield of the pentane derivative rises to about 12%, but  
if the addition and cooling are carefully controlled, the yield of  
cyclic compound is improved. The latter is slightly volatile in  
steam, and may be slowly removed in this way from the non-  
volatile pentane compound. In any case, the yields are poor, and  
the reaction cannot be fully explained. Ethyl pentane-ααα-tetra-  
carboxylate is a pleasant-smelling, viscous, colourless oil, b. p.  
210—215°/12 mm., and ethyl cyclobutane-1:1-dicarboxylate is a  
limpid, highly refractive oil with the odour of camphor, b. p.  
220—228° (compare Perkin, T., 1883—1891). The esters are con-  
verted into the amides and hydrazides by the action of ammonia  
or hydrazine in the usual way. *Pentane-ααα-tetracarboxylamide*  
forms soft prisms, m. p. 280°, and the *tetrahydrazide*,



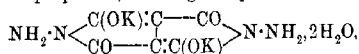
is a snowy powder, m. p. 200° (decomp.), which yields a *tetrahydro-*  
*chloride*, m. p. 200°, a *platinochloride*,  $\text{C}_3\text{H}_6\text{O}_4\text{N}_4\cdot 2\text{H}_2\text{PtCl}_6$ , and  
a *tetrabenzylidene* compound, m. p. 248°. The *tetra-azide* is an  
odourless, white powder, which melts under benzene at 50—55°, is  
comparatively stable when dry, but explodes on rubbing. The *tetra-*  
*anilide* is obtained from the azide as a white powder, m. p. 285°.  
The azide also changes into an impure carbamide derivative when  
boiled with water, and into an oily urethane on boiling with  
alcohol, the latter giving a distillate containing glutardialdehyde,  
 $\text{C}_3\text{H}_4(\text{CHO})_2$ , when boiled with dilute sulphuric acid. *cyclobutane-*

1:1-dicarboxylamide crystallises in long, rectangular prisms, m. p.  $268^{\circ}$ , and the dihydrazide,  $\text{CH}_2\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{C}(\text{CO}\cdot\text{N}_2\text{H}_3)_2$ , forms stout tablets or short needles, m. p.  $109-110^{\circ}$ , and yields a dihydrochloride, m. p.  $175-176^{\circ}$  (decomp.), a platinumchloride,  $\text{B}_2\text{H}_2\text{PtCl}_4$ , a dipicrate, yellow needles, m. p.  $185^{\circ}$ , a dibenzylidene compound, m. p.  $212-213^{\circ}$ , a disalicylidene compound, m. p.  $215^{\circ}$ , and a diisopropylidene compound, m. p.  $176-177^{\circ}$ . For the conversion of the dihydrazide into the diazide, the temperature of the mixture must be kept well below  $-5^{\circ}$ , otherwise evolution of carbon dioxide and nitrogen takes place and a deep red solution is obtained.

The diazide,  $\text{CH}_2\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{C}(\text{CO}\cdot\text{N}_3)_2$ , is a colourless, lachrymatory oil, which can only be kept when moist for a short time as it is decomposed by water. cyclobutane-1:1-dicarboxylanilide, m. p.  $214-215^{\circ}$ , and the di-p-toluidide, m. p.  $247^{\circ}$ , are obtained from the azide. The azide is hydrolysed to a considerable extent with the production of free hydrazoic acid when warmed with water or alcohol, but it also loses carbon dioxide and nitrogen, and when the product is acidified and distilled, cyclobutanone is found in the distillate. From the solution, cyclobutanonephenylhydrazone, a pure white, light mass of felted needles, or long needles from benzene, m. p.  $95-96^{\circ}$ , which can only be kept a few hours, and the stable semicarbazone, m. p.  $211-212^{\circ}$  (decomp.) (compare Demjanov and Dojarenko, A., 1908, i, 156), may be precipitated by adding the appropriate agents.

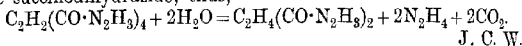
VI. [With HERMANN THIEMANN.]—Hydrazide and Azide of s-Ethanetetracarboxylic Acid.—Ethanetetracarboxytrihydrazide,  $\text{C}_2\text{H}_2(\text{CO}\cdot\text{N}_2\text{H}_3)_4$ , crystallises in slender needles, m. p.  $205^{\circ}$  (decomp.), and forms a tetrahydrochloride, m. p.  $145-148^{\circ}$  (decomp.), a tetrabenzylidene compound, m. p.  $242^{\circ}$ , a tetrasalicylidene compound, m. p.  $213-214^{\circ}$ , and a tetraisopropylidene compound,  $\text{C}_{18}\text{H}_{30}\text{O}_4\text{N}_8\cdot 4\text{H}_2\text{O}$ , m. p.  $255^{\circ}$ , which evolves dimethylketazine,  $\text{CMe}_2\cdot\text{N}\cdot\text{N}\cdot\text{CMe}_2$ , when heated at  $110^{\circ}$ . The conversion of the hydrazide into the tetra-azide (radiate groups of white crystals) only proceeds in the presence of an excess of hydrochloric acid which entails considerable loss of hydrazoic acid. The azide may be converted into the tetra-anilide, m. p.  $240-242^{\circ}$ , tetra-p-toluidide, m. p.  $236-237^{\circ}$ , and tetraurethane,  $\text{C}_2\text{H}_2(\text{NH}\cdot\text{CO}_2\text{Et})_4$ , white needles, m. p.  $268^{\circ}$ , the mother liquor from the latter preparation containing glyoxal. When the tetrahydrazide is warmed with water it changes into the yellow hydrazine salt of ethanetetracarboxytrihydrazide,  $\text{NH}_2\cdot\text{N}\langle\begin{smallmatrix}\text{CO} & \text{CH}\cdot\text{CO}\cdot\text{N}_2\text{H}_3 \\ \text{C}(\text{O}\cdot\text{N}_2\text{H}_3) & \text{C}\cdot\text{CO}\cdot\text{N}_2\text{H}_3\end{smallmatrix}\rangle$ , m. p.  $142^{\circ}$ , which reacts with acetone to form the triisopropylidene compound,  $\text{CMe}_2\cdot\text{N}\cdot\text{N}\langle\begin{smallmatrix}\text{CO}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}_2 \\ \text{CO}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}_2\end{smallmatrix}\rangle$ , m. p.  $138-140^{\circ}$  (with  $3\text{H}_2\text{O}$ , m. p.  $90-92^{\circ}$ ). This is converted into the tribenzylidene compound, m. p.  $193-194^{\circ}$ , by means of benzaldehyde, and then into the trihydrochloride, m. p.  $182-183^{\circ}$  (decomp.), by rubbing with

concentrated hydrochloric acid. The corresponding *triazide* is a very explosive, viscous oil, which may be converted into *ethane-tricarboxytriamide*,  $\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}\cdot\text{NHPh})_2$ , m. p. 223—224°, and *tri-p-toluidide*, m. p. 230°. The tetrahydrazide loses still more hydrazine residues when ground with bromine water or warmed with alcoholic iodine, the product being *ethanetetra-carb-oxydihydrazide*,  $\text{NH}_2\cdot\text{N}\langle\begin{smallmatrix} \text{CO}\cdot\text{CH}\cdot\text{CO} \\ \text{CO}\cdot\text{CH}\cdot\text{CO} \end{smallmatrix}\rangle\text{N}\cdot\text{NH}_2$ , which crystallises in highly refractive, glistening scales, m. p. 254—255°. This has both acidic and basic properties, forming a *dipotassium salt*,



pale yellow leaflets, m. p. 158°, a *dihydrazine salt*, m. p. 208°, a *diammonium salt*, m. p. 98°, which loses ammonia when kept, and a *hydrochloride*, m. p. 185—186° (decomp.). It also yields a *dibenzylidene* compound, m. p. 240—241°, a *disalicylidene* compound, m. p. 231—232°, a *diisopropylidene* compound, m. p. 261°, and a *tetra-acetyl* derivative, m. p. 202—203°. When treated with sodium nitrite and hydrochloric acid, the dihydrazide changes into *ethane-*

*tetracarboxydi-imide*,  $\text{NH}\langle\begin{smallmatrix} \text{CO}\cdot\text{CH}\cdot\text{CO} \\ \text{CO}\cdot\text{CH}\cdot\text{CO} \end{smallmatrix}\rangle\text{NH}$ , which crystallises in colourless leaflets, blackens at 265—270°, and forms a stable *disilver salt*,  $2\text{H}_2\text{O}$ . When boiled with water for a few hours, the tetra- or tri-hydrazides lose carbon dioxide as well as hydrazine and give succinodihydrazide, thus,



J. C. W.

**The Evolution of Proteins.** E. L. KENNAWAY (*Chem. News*, 1920, 120, 13—16).—After discussing the amino-acids which have been established as occurring commonly in proteins, the author draws attention to their very limited number, but great diversity, as regards structure. He then goes on to consider whether the simplest plants, for example, bacteria, yeasts, contain all these amino-acids present in the higher plants, and, taking the information available, shows that, with the exception of hydroxyproline, the presence or absence of which is not established, all the seventeen amino-acids considered are present in one or other of the five bacteria, yeast and mould, which have been examined. The two doubtful occurrences are serine and cystine. The author then discusses the bearing of these results on evolution, particularly on that of the higher animals, which are dependent on plant life for some of their essential amino-acids.

W. G.

**The Hydrolysis of Proteins in the Presence of Extraneous Materials and on the Origin and Nature of the "Humin" of a Protein Hydrosol.** R. A. GORTNER (*Science*, 1918, 48, 122—124; from *Physiol. Abstr.*, 1920, 4, 466).—A strong criticism of McHargue's statements regarding protein hydrolysis (compare A., 1918, ii, 280).

W. G.

**Action of Furfuraldehyde and Dextrose on Amino-acids and Protein Hydrolysates.** C. T. DOWELL and PAUL MENAUL (*J. Biol. Chem.*, 1919, **40**, 131—136).—It was observed that when whole plants, including the seed, are hydrolysed, a large amount of furfuraldehyde is given off, and that an unusually high percentage of humin nitrogen is obtained. No evidence of a reaction between glycine and furfuraldehyde was obtained, but there was an indication that reaction occurred with tyrosine and cystine. Only a slight amount of the humin nitrogen is due to adsorption. There is reaction between the hydrolysates of proteins and furfuraldehyde, which is particularly marked when the reaction takes place in neutral or acid solution. The greatest loss of amino-nitrogen occurs, however, when dextrose is present during hydrolysis, and it is therefore concluded that dextrose reacts directly with the amino-acids, and not through the intermediate formation of furfuraldehyde. Complete hydrolysis of proteins may be effected by heating in 10% hydrochloric acid for three hours at 20 lb. pressure.

J. C. D.

**Hydrolysis of Stizolobin, the Globulin of the Chinese Velvet Bean, *Stizolobium niveum*.** D. BREESE JONES and CARL O. JOHNS (*J. Biol. Chem.*, 1919, **40**, 435—448).—The globulin of the Chinese velvet bean has been hydrolysed and the percentages of the constituent amino-acids determined: 77.21% of the total protein was isolated as amino-acids and ammonia. Aspartic acid was determined both by the usual ester method and by Dakin's recently published process (Dakin, A., 1919, i, 150). The former method yielded 5.7% and the new process 9.23%. 2.81% of the recently discovered hydroxyglutamic acid was also obtained.

J. C. D.

**Solubility of Casein in Dilute Solutions of Sodium Chloride and its Dependence on the Hydrogen Ion Concentration.** SIGFRID RYD (*Arkiv. Kem. Min. Geol.* 1917, **7**, No. 1, 1—15).—The solubility of casein in dilute solutions of sodium chloride has been determined for thirty-two concentrations at 18—20°. The casein in weighed quantity was placed in a cylindrical vessel fitted with stirrer, thermometer, and two burettes. A quantity of a standard solution of sodium hydroxide, sufficient to dissolve the casein, but not an excess, was added, and the mixture stirred until solution had occurred. Then from one of the burettes standard hydrochloric acid was added until an opalescence was produced. The amount of sodium hydroxide taken in the first place was so chosen that the hydrochloric acid necessary to produce opalescence was slightly more than equivalent to the sodium hydroxide, the excess of acid was neutralised, and the casein redissolved by the addition of sodium hydroxide from the other burette. This process was continued until the acid and alkali, when exactly equivalent, just produced an opalescence. Hence the concentration of the solution on casein and sodium chloride was known. The solubility of casein in sodium chloride solution rises with increase in

the concentration of the sodium chloride to a maximum, which is reached with 0.1150*N*-sodium chloride. The following are the extreme values: 0.0365*N*-NaCl dissolves 0.64 mg. per c.c., 0.1150*N*-NaCl dissolves 3.46 mg. per c.c., and 0.2725*N*-NaCl dissolves 1.32 mg. per c.c. The hydrogen-ion concentration of each saturated solution was determined at 21°, and it is found that this quantity is practically constant at  $5.13 \times 10^{-6}N$ , from which it follows that opalescence in solutions of casein occurs when the hydrogen-ion concentration has the above value and this lies very near the iso-electric point, which has a value  $1.1 \times 10^{-4}$ — $7.9 \times 10^{-5}$ .

J. F. S.

### Hæmocyanin. I. Recrystallisation of Oxyhæmocyanin.

ATREU D. CRAIFALEANU (*Boll. Soc. Nat. Napoli.*, 1918, **31**, 88—99).—The author describes the crystallisation of hæmocyanin from the blood of *Octopus vulgaris*, *O. macropus*, and *Eledone moschata*, following the methods described by Hofmeister and by Hopkins and Pinkus for the crystallisation of egg-albumin.

The hæmocyanin derived from the blood of *O. vulgaris* may crystallise in three different forms: short needles, rosettes of needles, and relatively large crystals, which, from their appearance under the microscope, the author terms "projectile" crystals. These forms vary with the conditions of crystallisation. The hæmocyanin from *O. macropus* was obtained in long, needle-shaped crystals. On allowing the glass containing the crystals and mother liquor to remain for some time, the crystals become insoluble, and this modification is termed *parahæmocyanin*. The pigment from the blood of *E. moschata* crystallises in needles. The so-called "projectile" crystals are characteristic of the hæmocyanin from *O. vulgaris*.

J. C. D.

### Crystalline Salts of Uridinephosphoric Acid. P. A.

LEVENE (*J. Biol. Chem.*, 1919, **40**, 395—398. Compare A., 1918, i. 130).—The normal ammonium salt is readily prepared from the brucine salt, and crystallises in heavy, elongated prisms, decomp. 185° (uncorr.). In aqueous solution it has  $[\alpha]_D^{20} + 21.0^\circ$ , and crystallises with  $11H_2O$ . The ammonium hydrogen salt crystallises in long, prismatic needles,  $[\alpha]_D^{20} + 13.0^\circ$ , contracts at 210° (corr.), decomp. at 242° (corr.). Normal lead salt, long needles. Brucine salt,  $C_{12}H_{13}O_4N_3P(C_{23}H_{29}O_4N_2) \cdot 7H_2O$ ,  $[\alpha]_D^{20} - 20.0^\circ$  (in very dilute solution). Air-dried substance effervesced at 185° (corr.), and contracted and melted without further decomposition at 195° (corr.).

J. C. D.

### Crystalline Guanylic Acid. P. A. LEVENE (*J. Biol. Chem.*,

1919, **40**, 171—174).—The crude brucine salt of guanylic acid was converted into the ammonium salt and precipitated from aqueous solution with neutral lead acetate. The solution obtained after removal of lead from the precipitate yielded, on concentration under diminished pressure, a crystalline substance. Analysis corresponded

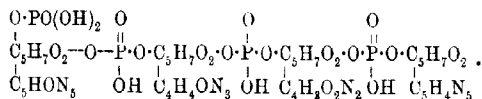
with the formula  $C_{10}H_{14}O_8N_{5.5}H_2O$ ,  $[\alpha]_D^{20}$  in aqueous solution  $-7.5^\circ$ . In 5% aqueous ammonia,  $[\alpha]_D^{20} -43.5^\circ$ . In 10% hydrochloric acid it was optically inactive. The substance had all the properties of guanylic acid. It gelatinised in the presence of mineral impurities and turned brown at  $208^\circ$ . The brucine salt,  $C_{56}H_{64}O_{16}N_8 \cdot 7H_2O$ , contracted at  $217^\circ$ , melted at  $233^\circ$ , and effervesced at  $240^\circ$ ;  $[\alpha]_D^{20} -26.0^\circ$  in 35% alcohol. J. C. D.

**The Structure of Yeast-Nucleic Acid. IV. Ammonia Hydrolysis.** P. A. LEVENE (*J. Biol. Chem.*, 1919, **40**, 415—424).

—The original graphic representation of the entire molecule of yeast-nucleic acid had only an arbitrary schematic sense (compare Levene and Jacobs, A., 1909, i, 620, 686; 1911, i, 96, 510). The views as to structural formulæ advanced by Jones (A., 1917, 232, 233, 596, 597) and by Thannhauser (A., 1914, i, 1015; Thannhauser and Dorfmueller, A., 1918, i, 47) and the evidence adduced in their support are considered.

Nucleic acid was hydrolysed in a 2.5% aqueous ammonia solution for one hour at  $100^\circ$ , a milder treatment than that employed by either Jones or Thannhauser. It is proved that the adenine-uridine dinucleotide is a mixture of two mononucleotides. The fraction originally regarded by Jones as a guanine-cytosine dinucleotide was found to consist principally of guanosinephosphoric acid, together with a small proportion of uridinephosphoric acid. The present findings nullify the experimental evidence in support of the theories of Jones and Thannhauser. From the theoretical point of view, the theory of Thannhauser is weak because it assumes a carbon to carbon linking, which is a very strong type of union, whereas the polynucleotide is readily dismembered into mononucleotides. The ether linking accepted by Jones is also a very firm union.

On the basis of considerations such as these the linking of the nucleotides could be expressed most simply in the following way:



For the present this formula expresses the facts known about the structure of yeast-nucleic acid. Whether it will require alteration or not, it is certain that the polynucleotide structure of yeast-nucleic acid is definitely established. J. C. D.

**The Combination of Enzyme and Substrate. I. Estimation of Pepsin. II. The Effect of the Hydrogen Ion Concentration.** JOHN H. NORTHRUP (*J. Gen. Physiol.*, 1919, **2**, 113—122).—The change in the conductivity during the digestion of egg-albumin by pepsin affords a convenient and accurate method for the estimation of pepsin. The changes in conductivity do not follow the actual rate of digestion, but the percentage change in conductivity is constant for a given quantity of pepsin, irrespective of the absolute value of the original conductivity. It was found

that the maximum change occurred in strong solutions of egg-albumin titrated to  $p_H$  2.6 with hydrochloric acid. By this process it is possible to determine quantitatively the amount of pepsin removed from solution by various substances.

A series of experiments with substances such as starch, calcium sulphate, agar, kaolin, blood-charcoal, caseinogen, and egg-albumin gave results which indicate that the removal of pepsin from solution is not purely a matter of surface, but that it is dependent in some way on the substance itself. That is, the equilibrium reached is independent of the size of the particles, and therefore of their surface. This would indicate that the process is either one of solution, in which case the law of partition-coefficients should be found to hold, or of chemical combination, in which case the law of mass action should apply.

Preliminary experiments indicate that the process follows the law of partition-coefficients.

There is a decided optimum hydrogen-ion concentration for the combination of pepsin with its substrate corresponding with the optimum reaction for digestion. It is suggested that the combination of pepsin with its substrate, and hence the rate of digestion, is governed by the quantity of ionised protein present. J. C. D.

**The Different Actions of Pepsin and Chymosin on Acid Solutions of Syntonin.** OLOF HAMMARSTEN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 7, 1—13).—In previous papers (compare A., 1918, i, 459, 510) the author has put forward evidence in support of assigning separate identities to chymosin and pepsin. Further support to his views is given by the experiments detailed in the present paper, syntonin obtained from fish or horseflesh being used in place of acid and alkali legumin (A., 1918, i, 510). The method of experiment was similar to that previously detailed, and all the results indicate that chymosin acts on syntonin, forming albumoses, at an acid concentration at which pepsin is inactive.

T. S. P.

**Catalase.** EIICHI YAMAZAKI (*J. Tokyo Chem. Soc.*, 1919, 40, 514—522).—The author has previously deduced an equation (*ibid.*, 35 and 36) by which it is possible to describe the course of the reaction between catalase and hydrogen peroxide at any temperature and any initial concentrations by using the temperature-coefficient and the value of  $k$  at 18°. He now finds that, contrary to Evans's statement (A., 1907, i, 456), even with a range of concentration from 1 to 80,  $k/E_0$  is constant provided the hydrogen-ion concentration is kept constant. Blood catalase, prepared by the method of Senter (A., 1903, ii, 661), is diluted to less than 1%, 20 c.c. of 0.02N-sodium hydrogen carbonate are added to each solution of the enzyme, the volume is made up to 130 c.c. at 25°, and 20 c.c. of 0.028N-hydrogen peroxide are added. The estimations are made in a current of carbon dioxide.

The author discusses the kinetics of catalase action, and is of opinion that the action is purely chemical.

CHEMICAL ABSTRACTS.

**Urease and the Radiation Theory of Enzyme Action. IV.**

H. P. BARENDRECHT (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 22, 126—138. Compare A., 1919, i, 604; this vol., i, 102).—A continuation and completion of previous work. The accelerating action observed with urease and attributed by previous experimenters to carbon dioxide is shown to be non-existent. Ammonium carbonate and carbon dioxide form a powerful buffer mixture which can maintain a constant  $P_H$  value, the essential condition for constant enzyme activity in a urea solution during hydrolysis by urease. The estimation of initial velocities of hydrolysis, equal concentrations of urease being allowed to act on different concentrations of urea at constant  $P_H$  and  $T$  values, produces results which appear inexplicable without the radiation theory. The lower the value of  $P_H$  the more the initial velocities increase with increase in the urea concentration. With high  $P_H$  values there is first an increase and then a decrease on raising the urea concentration. These facts are strictly in accordance with the radiation hypothesis. The urease radiation, weakened by spreading or in any other way, may effect synthesis. This is indicated by the fact that at high  $P_H$  values, where the urease is shown to be decaying, reversion of an hydrolysis has been observed. From the last fact it is deduced that outside the sphere of hydrolytic action around a urease molecule there must be a region of radiation, weakened by spreading, and therefore of synthesis. This is confirmed by the fact that on diluting the urease concentration beyond a certain value, its specific activity is decreased. From this it is evident that the synthetic action of urease, which is not decaying, can only come into play when the spheres of hydrolytic action do not intersect one another. It is shown experimentally that in any urease solution in which the enzyme is decaying through the combined action of alkalinity, temperature, and time, a synthesis of urea from ammonium carbonate, proportional to the urease concentration, is observed. A description of an apparatus for determining the concentration of hydrogen and hydroxyl ions is included in the paper. J. F. S.

**Cyanodiphenylarsine.** GIUSEPPE STURNIOLO and GIACOMO BELLINZONI (*Boll. Chim. Farm.*, 1919, 58, 409—410\*).—*Cyanodiphenylarsine*,  $\text{AsPh}_2\text{CN}$ , crystallises in almost colourless, apparently monoclinic plates, m. p.  $35^\circ$ , having the odour of both garlic and bitter almonds, hydrogen cyanide being liberated readily by the action of moist air; its odour irritates the nasal mucus, provoking sneezing. By treatment with aqueous or alcoholic alkali hydroxide, or by heating with water, or by distillation either in a current of steam or under reduced pressure (100 mm.), it is converted into diphenylarsine oxide,  $(\text{AsPh}_2)_2\text{O}$ . When treated either with concentrated nitric acid on the water-bath or with 2% hydrogen peroxide, or with bromine water in the cold, it yields diphenylarsinic acid. Both cyanodiphenylarsine and diphenylarsine oxide, containing tervalent arsenic, are transformed into diphenylarsinic acid, in

\* and *Gazzetta*, 1919, 49, ii, 326—327.



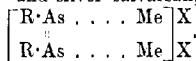
which the arsenic is quinquivalent, by the traces of hydrogen peroxide sometimes occurring as impurities in ether and in light petroleum. The alkali salts of diphenylarsinic acid are soluble, whereas the iron salt forms a very fine, white, insoluble powder and decomposes when heated.

T. H. P.

**Tetraphenyldiarsine.** C. W. PORTER and PARRY BORGSTROM (*J. Amer. Chem. Soc.*, 1919, **41**, 2048—2051).—The authors have prepared tetraphenyldiarsine in a pure state from the oxide by the method of Michaelis and Schulte (compare A., 1883, 187), and distributed it into sealed glass tubes without allowing it to come into contact with air. So prepared, when exposed to air it oxidises to diphenylarsinic acid and tetraphenyldiarsine oxide, but is not spontaneously inflammable, as reported by Michaelis (compare A., 1902, i, 515). In benzene solution it gradually absorbs oxygen. In similar solution it rapidly absorbs iodine, giving a crystalline iodo-compound, m. p.  $36^{\circ}$ , which is probably diphenyliodoarsine. Its vapour pressure at  $200^{\circ}$  is about 1 mm., and at  $300^{\circ}$  in a vacuum it decomposes, giving arsenic and triphenylarsine, and consequently its molecular weight in the state of vapour cannot be determined. Molecular weight determinations by the cryoscopic method in naphthalene indicate that tetraphenyldiarsine is associated at the freezing point of naphthalene.

W. G.

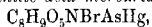
**The Constitution of Arseno-metallic Compounds.** P. KARRER (*Ber.*, 1919, **52**, [B], 2319—2324).—In reply to Kelle (*Deut. med. Woch.*, 1918, 1177) and Binz, Bauer and Hallstein (*Arbb. aus Inst. exp. Therapie Georg Speyer Haus*, 1919, **25**, 45), the author maintains the correctness of the views advanced by Ehrlich and Karrer (A., 1916, i, 95), that the metal in complex salts, such as copper- and silver-salvarsan, is directly united to the arsenic atom, thus,



H. W.

**Chemotherapeutic Studies on Organic Compounds containing Mercury and Arsenic.** GEORGE W. RAIZISS, JOHN A. KOLMER, and JOSEPH L. GAVRON (*J. Biol. Chem.*, 1919, **40**, 533—552).—The following are described: 3-Nitroarsanic acid mercuriacetate,  $\text{OAc} \cdot \text{Hg} \cdot \text{C}_6\text{H}_2(\text{NO}_2)(\text{NH}_2)_2 \cdot \text{AsO}(\text{OH})_2$ , bright yellow powder soluble in dilute sodium hydroxide on warming. 3-Nitro-4-hydroxyphenylarsinic acid mercuriacetate,  $\text{C}_6\text{H}_3\text{O}_2\text{NAsHg}$ , yellow powder soluble in dilute sodium hydroxide. 3:5-Dinitro-4-hydroxyphenylarsinic acid mercuriacetate,  $\text{C}_6\text{H}_2\text{O}_2\text{N}_2\text{AsHg}$ , bright yellow powder partly soluble in dilute sodium hydroxide. 3-Amino-4-hydroxyphenylarsinic acid mercuriacetate,  $\text{C}_6\text{H}_4\text{O}_2\text{NAsHg}$ , brown powder soluble in dilute sodium hydroxide; the solution decomposes on keeping, with deposition of metallic mercury. 3:5-Diamino-4-hydroxyphenylarsinic acid mercuriacetate,  $\text{C}_6\text{H}_3\text{O}_2\text{N}_2\text{AsHg}$ , dark brown powder soluble in very dilute sodium hydroxide; the solution

decomposes, with formation of metallic mercury. 4-Carboxyphenyl-arsinic acid mercuriacetate,  $C_6H_5O_7AsHg$ , cream-coloured powder insoluble in dilute sodium hydroxide, soluble in dilute hydrochloric acid, concentrated sodium chloride solution, and in glacial acetic acid on warming. Diacetyl-3:5-diamino-4-hydroxyphenylarsinic acid mercuriacetate,  $C_{18}H_{15}O_8N_2AsHg$ , grey powder soluble in dilute sodium hydroxide to form a brown solution, from which mercury is deposited. 3-Bromoarsanilic acid mercuriacetate,



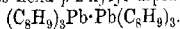
white powder soluble in dilute sodium hydroxide, warm glacial acetic acid, and 10% hydrochloric acid. 3-Bromo-oxalylarsanilic acid mercuriacetate,  $C_{10}H_9O_5NBrAsHg$ , white powder soluble in dilute sodium hydroxide; the solution deposits metallic mercury on keeping.

All the above compounds are insoluble in the usual organic solvents. The presence of the arsinic acid group in the molecule of organic compounds apparently does not interfere with the entrance of the mercury group. As a class, this type of compound is comparatively stable in alkaline solution, the splitting off of mercury occurring only in compounds containing an amino-group. The toxic effect on the animal body appears to be caused mainly by the mercury group. These new compounds were not found to be superior to the ordinary organic mercury compounds as regards curative influence in experimental trypanosomiasis and germicidal effect in vitro.

J. C. D.

**Lead Triaryl, a Parallel to Triphenylmethyl.** ERICH KRAUSE and MARIA SCHMITZ (*Ber.*, 1919, **52**, [B], 2165—2170).—Indications of the formation of unsaturated organo-derivatives of lead, in which the metal is attached to carbon atoms by fewer than four valencies, have been previously observed, but the isolation of such substances has hitherto been impossible. The authors have succeeded in preparing lead tri-*p*-2-xylyl in the crystalline condition, and have shown that unsaturated derivatives are also formed to a greater or less extent by the action of magnesium phenyl or *p*-tolyl bromide on lead dichloride.

Lead tri-*p*-2-xylyl,  $Pb(C_6H_3Me_2)_3$ , is prepared by the addition of finely powdered lead dichloride to an ethereal solution of the calculated quantity of magnesium *p*-2-xylyl bromide; the bulk of the dichloride dissolves to a brownish-yellow or chestnut-brown solution of the diaryl compound, which gradually at the ordinary temperature, but more rapidly when heated, deposits lead and yields the lead triaryl. The substance forms a pale yellowish-green, heavy, crystalline powder which, under the microscope, appears to be formed of colourless, well-developed rhombs. Determinations of the molecular weight by the cryoscopic method in benzene solution indicate the formula  $[(C_6H_3)_3Pb]_2$ , so that the compound may possibly be regarded as hexa-*p*-2-xylyl diplumban,



The colour of the substance, however, points to a feeble union of

the lead atoms and to the possibility of dissociation under the influence of light. Probably the lead atoms are united in much the same manner as the methane carbon atoms of the triaryl methyls. As is to be expected, the substance is readily attacked by chemical reagents; thus, when treated with bromine in pyridine solution at  $-40^{\circ}$ , it gives *lead tri-p-2-xylyl bromide*, four-sided leaflets, m. p.  $177^{\circ}$ , whilst in chloroform solution at  $-10^{\circ}$  it yields *lead di-p-2-xylyl dibromide*, colourless, shining rods, m. p.  $120^{\circ}$ . Lead tri-p-2-xylyl is remarkably stable towards air, and is not oxidised either in the solid state or in solution, although in the latter condition it is rapidly and completely decomposed on exposure to light. It is not sensitive to rise of temperature, and decomposition does not occur until  $220^{\circ}$ ; for this reason, attempts to obtain *lead tetra-p-2-xylyl* by the action of magnesium p-2-xylyl bromide on lead chloride at elevated temperatures were unsuccessful, but the compound was readily prepared from lead tri-p-2-xylyl bromide and the Grignard reagent; it forms colourless, rectangular plates, m. p.  $255^{\circ}$ , which decompose above  $270^{\circ}$ , with separation of lead.

H. W.

**Mixed Lead and Tin Aryls and Aryl Alkyls and their Application to the Synthesis of Organo-compounds of Silver. Examples of the Influence of Symmetry on the Properties of Chemical Compounds.** ERICH KRAUSE and MARIA SCHMITZ (*Ber.*, 1919, 52, [B], 2150—2164).—The conversion of the readily accessible lead aryl monohaloids and tin aryl monohaloids (*A.*, 1918, i, 415) into mixed aryl and aryl alkyl compounds is described. Asymmetry in the latter appears to impart to the compounds lower m. p. and greater solubility and chemical activity, which is explained by the assumption that the metallic atom is more completely protected from contact with a reagent by the symmetrical union with, for example, four phenyl groups, whilst with unlike groups spaces are left, through which the reagent can penetrate. The lead and tin aryls or aryl alkyls react with a cold alcoholic solution of silver nitrate, yielding bright yellow precipitates, which could not always be isolated in a pure condition, but which are shown in the cases of lead and tin triphenylethyls to have the composition  $2\text{PhAg}, \text{AgNO}_3$ .

*Mixed Lead Aryls and Aryl Alkyls.*—The compounds are prepared by the addition of lead triphenyl bromide to an ethereal solution of the magnesium aryl bromide, and are isolated in the usual manner. Unnecessarily protracted heating and long exposure of the crude products or their solutions to light and the air of the laboratory are to be avoided. The yields are almost quantitative. The following substances are described: *lead triphenyl p-tolyl*, hair-like needles, m. p.  $125.5^{\circ}$ ; *lead triphenyl p-2-xylyl*, transparent crystals, m. p.  $104.5^{\circ}$ ; *lead triphenyl m-4-xylyl*, rods arranged in clusters, m. p.  $111.5-112^{\circ}$ ; *lead triphenyl p-phenetyl*, small, shining needles, m. p.  $119-120^{\circ}$ ; *lead triphenyl a-naphthyl*, colourless needles grouped in rosettes, m. p.  $101^{\circ}$ ; *lead triphenyl cyclo-*

*heptyl*, m. p. 119°; *lead triphenyl ethyl*, needles, m. p. 42°,  $n_D^{20}$  1.62628,  $D_4^{20}$  (vac.) 1.5885; *lead diphenyl di- $\alpha$ -naphthyl* (from lead diphenyl dibromide and magnesium  $\alpha$ -naphthyl bromide), microscopic prisms, m. p. 197°; *lead di- $\alpha$ -naphthyl diethyl*, intergrown prisms, m. p. 116°.

*Mixed Tin Aryls and Aryl Alkyls*.—These are prepared from tin triphenyl chloride and excess of magnesium aryl or alkyl haloid in almost quantitative yield. The following substances are described: *tin triphenyl p-tolyl*, small, slender needles, m. p. 124°; *tin triphenyl p-2-xylyl*, coarse, six-sided plates, m. p. 100.5°; *tin triphenyl  $\alpha$ -naphthyl*, colourless prisms, m. p. 125°; *tin triphenyl methyl*, large, shining rhombs, m. p. 60°,  $D_4^{20}$  (vac.) 1.3113,  $n_D^{20}$  1.6001,  $n_D^{25}$  1.60661,  $n_D^{35}$  1.62351,  $n_D^{45}$  1.63831; *tin triphenyl ethyl*, ice-like crystals, m. p. 56°,  $D_4^{20}$  (vac.) 1.2953,  $n_D^{20}$  1.59917,  $n_D^{25}$  1.60542,  $n_D^{35}$  1.62236; *tin tetra- $\alpha$ -tolyl* (by action of a large excess of magnesium  $\alpha$ -tolyl bromide on a suspension of the etherate of stannic chloride), white, crystalline powder, m. p. 158–159°.

*Action of Mixed Lead and Tin Aryls on Silver Nitrate and Mercuric Chloride*.—*Silver phenyl silver nitrate*,  $2\text{PhAg}, \text{AgNO}_3$ , is prepared by the cautious addition of a solution of lead triphenyl ethyl in absolute alcohol to an alcoholic solution of silver nitrate. It forms a canary-yellow, amorphous powder resembling cadmium sulphide in shade. The colour deepens rapidly when the substance is heated until decomposition occurs at about 100°, the exact temperature depending both on the rate of heating and on the age of the preparation. It explodes when heated in a test-tube. The colour is practically unchanged after twelve hours in complete darkness, but darkens within a few minutes on exposure to diffused light. Similarly, lead triphenyl ethyl and mercuric chloride yield mercury phenyl chloride, leaflets, m. p. 250°. Tin triphenyl ethyl gives silver phenyl silver nitrate and mercury phenyl chloride with silver nitrate and mercuric chloride respectively, the products being identical with those prepared from the lead compound. Lead triphenyl *p*-phenetyl and silver nitrate yield a product which closely resembles the silver compound described above, but does not appear to be homogeneous. Lead tetraphenyl, tetra-*p*-tolyl, and tetra-*p*-2-xylyl are not acted on by cold alcoholic silver nitrate solution, but the solid compounds become grey, owing to the gradual reduction of the silver nitrate on protracted boiling of the solution. Lead triphenyl *p*-tolyl, triphenyl *p*-2-xylyl, and triphenyl *m*-4-xylyl have no action in dilute solution, or only cause a yellow coloration; with excess of concentrated silver nitrate solution, immediate precipitates closely resembling silver phenyl silver nitrate are formed, which give a colourless solution in the boiling solvent, and then yield a silver mirror and a brownish-yellow precipitate. Lead triphenyl  $\alpha$ -naphthyl, diethyl dinaphthyl, and triphenyl cyclohexyl yield immediate precipitates, even in dilute solution, which are very similar to one another in appearance and reactions, except in colour of the naphthyl compounds, which is orange-yellow; the latter substances yield naphthalene when treated with hydrochloric acid.

Lead diphenyl di- $\alpha$ -naphthyl does not react with alcoholic silver nitrate.

The aromatic tin compounds react less readily than the corresponding lead compounds. Tin tetraphenyl does not react; tin triphenyl *p*-tolyl and triphenyl *p*-2-xylyl do not act in cold solution, and cause reduction when boiled. Tin triphenyl phenetyl gives a yellow precipitate after a few seconds, whilst tin triphenyl methyl, like the ethyl compound, gives an immediate precipitate of silver phenyl silver nitrate, which becomes black when warmed.

According to the literature, the lead alkyls immediately reduce silver nitrate; the authors' hypothesis, that very unstable silver alkyls are formed as intermediate products, is confirmed by the observation that yellow precipitates are formed, which are stable at  $-30^\circ$  for several seconds, and at  $-80^\circ$  for several minutes.

H. W.

## Physiological Chemistry.

**Analyses of Blood Gases. III. The Permeability of Human Erythrocytes to Chlorions.** H. STRAUB and KLOTHILDE MEIER (*Biochem. Zeitsch.*, 1919, **98**, 205—228. Compare A., 1919, i, 53).—Blood corpuscles suspended in a physiological sodium chloride solution were subjected to the influence of various concentrations of carbon dioxide. It was found that the corpuscles acted as "buffers" towards carbon dioxide. The hydron concentration of the inside of the cells exceeded  $P_H=7.00$  only when the sodium chloride solution in which the corpuscles were suspended reached an hydron concentration of  $P_H=6.67$ . This is, no doubt, brought about by the alteration in the colloidal condition of the cell membrane. The change in the hydron concentration was found to be independent of the concentration of Cl and Na ions of the solution in which the corpuscles are suspended as long as a certain minimum of these ions was assured and the solution made isotonic. In hypertonic 0.2 molar salt solutions, the change in the corpuscles was brought about at the same hydron concentration, namely,  $P_H=6.67$ . In a hypertonic 0.102 molar solution, on the other hand, the change took place earlier.

S. S. Z.

**Analyses of Blood Gases. IV. The Influence of Alkali Ions on the Hæmoglobin and Cell Membrane.** H. STRAUB and KLOTHILDE MEIER (*Biochem. Zeitsch.*, 1919, **98**, 228—256).—The influence of alkali ions on the electrical charge of hæmoglobin and on the permeability of the membrane of human erythrocytes to these ions has been studied. The membrane becomes permeable to the various ions at the following hydron concentrations: Li and Na at  $P_H=6.67$ , K at  $P_H=6.8$ , Rb at  $P_H=6.92$ , Cs at  $P_H=7.06$ . The hæmoglobin loses its charge on the addition of the alkali ions

at the following hydron concentrations: Na and K at  $P_H=7.00$ , Rb at  $P_H=7.22$ , Cs at  $P_H=7.34$ . The membrane becomes permeable to ammonium ions in low concentrations at  $P_H=7.48$ . Higher concentrations of these ions require a higher hydron concentration before the membrane becomes permeable to them. The action of ammonium ions on the charge of the hæmoglobin is similarly influenced by the concentration of the ions. The analogy between the permeability of the cell membrane to the alkali ions, and the precipitation of colloids by means of these ions, is pointed out. The bearing of the adsorption theory on the permeability of the cell membranes to alkali ions is also discussed.

S. S. Z.

**Influence of High Temperatures and Dilute Alkalis on the Antineuritic Properties of Food.** AMY L. DANIELS and NELLIE I. MCCLURG (*J. Biol. Chem.*, 1919, **37**, 201—213).—The results obtained by these authors are not in accord with those reported by McCollum and Simmonds (*ibid.*, 1918, **33**, 55). It appears improbable that the commercial canning of foods is responsible for a serious destruction of the antineuritic vitamine, and the warning sounded by Chick and Huma (*Proc. Roy. Soc.*, 1917, [B], **90**, 60) is regarded as unfounded.

J. C. D.

**The Vitamines of Green Foods.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (with co-operation of EDNA L. FERRY and ALFRED J. WAKEMAN) (*J. Biol. Chem.*, 1919, **37**, 187—200).—Dried yeast is somewhat more than four times as efficient as dried spinach leaves when used as a source of the water-soluble vitamine. These leaves, however, appear to be a rich source of fat-soluble A. The values of cabbage, lucerne, clover, and timothy plants in supplying the water-soluble accessory substance are of the same order as that of spinach, but the experiments are not regarded as complete.

Very small amounts of lucerne, clover, and timothy plants will supply sufficient fat-soluble A for the growth of young rats. Emphasis is therefore laid on the importance of fresh green vegetables in the human dietary.

J. C. D.

**Identity of the Water-soluble Growth-promoting Vitamines and the Antineuritic Vitamine.** H. H. MITCHELL (*J. Biol. Chem.*, 1919, **40**, 399—413).—The author reviews the literature dealing with the distribution, properties, and character of these two substances, and forms the opinion that there is as yet insufficient evidence to assume that they are identical.

J. C. D.

**Formation of Urea by the Placenta.** FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1919, **37**, 105—112).—Formation of urea by the placenta may be conclusively demonstrated, although the processes leading up to its production can only be surmised.

J. C. D.

**Physical Properties and Chemical Composition of Human Amniotic Fluid.** DOKO UYENO (*J. Biol. Chem.*, 1919, **37**, 77—101).—The human amniotic fluid at the end of pregnancy

always contains coagulable albumins (an average of 0.226%, inclusive of mucin). The quantity of mucin was too small to be estimated. Peptones and proteoses were not found. Approximately 0.003% of ammonia and 0.0323% of urea were found, together with very small amounts of uric acid and creatine, but creatinine and hippuric acid were absent. Cholesterol is also a component of the human amniotic fluid. J. C. D.

**The Effect of Pyretics and Antipyretics on Catalase Production.** W. E. BURGE (*J. Pharm. expt. Ther.*, 1919, 14, 121—130).—Tetrahydro- $\beta$ -naphthylamine, adrenaline, caffeine, and sodium chloride stimulate the alimentary glands, particularly the liver, to an increased output of catalase; this fact is offered in explanation of the increased oxidation produced by these substances, and hence of the accompanying fever, in so far as the increased heat production is involved in this. Chloroform decreases catalase both by decreasing its output from the liver and by direct destruction of this enzyme. Ether decreases catalase principally by direct destruction of the enzyme without disturbing the liver function so much as does chloroform. Acetanilide, quinine, and phenacetin produce a slight decrease in catalase by decreasing its output from the liver. Chloroform and ether lower temperature in so far as decreased oxidation is involved in this by decreasing catalase, the enzyme principally responsible for oxidation in the body. The fact that acetanilide, quinine, and phenacetin have little or no effect in decreasing catalase suggests that their mode of action in lowering temperature is not due to a decrease in oxidation. J. C. D.

**The Carnosine Content of Normal and Pathological Human Cardiac Muscles.** F. BUBANOVIĆ (*Biochem. Zeitsch.*, 1918, 92, 125—129).—The carnosine content of the human heart is very constant, and is not influenced either by hypertrophy or atrophy of the muscles. The average content is 0.25%. The carnosine was determined when possible, both by the diazo and the copper colorimetric methods. S. S. Z.

**Bioluminescence. X. Production of Carbon Dioxide during Luminescence of Cypridina Luciferin.** E. NEWTON HARVEY (*J. Gen. Physiol.*, 1919, 2, 133—135).—All luminous animals require oxygen for luminescence, but there has previously been some doubt as to whether carbon dioxide is given off as a result of this phenomenon. A brilliant luminescence results when a small amount of luciferase solution is added to a solution of *Cypridina* luciferin (A., 1919, i, 299), so that it should be possible to ascertain whether this process is accompanied by a liberation of carbon dioxide. The results of experiments indicate that the oxidation of luciferin which is responsible for luminescence is not to be compared with the reactions in cells giving rise to the carbon dioxide of respiration. As previously suggested by the author, the process is probably similar to the oxidation of a leuco-dye (A., 1919, i, 299). J. C. D.

**Bioluminescence. XI. Heat Production during Luminescence of Cypridina Luciferin.** E. NEWTON HARVEY (*J. Gen. Physiol.*, 1919, 2, 137—143).—The heat change during the oxidation of luciferin by luciferase was investigated in order to ascertain the nature of the luminescent reaction. The change observed was so small that it is estimated that 1 gram of luciferin develops less than 0.1 cal. during the oxidation process accompanying luminescence. This clearly differentiates this type of reaction from those such as the oxidation of dextrose, 1 gram of which will give 4000 cal. It therefore appears probable that no carbon dioxide is produced during the oxidation of luciferin, and that the process is one more closely resembling the oxidation of leuco-methylene-blue (compare preceding abstract). J. C. D.

**Physiology of Phosphorus and Calcium Metabolism as Related to Milk Secretion.** EDWARD B. MEIGS, N. R. BLATHERWICK, and C. A. CARY (*J. Biol. Chem.*, 1919, 37, 1—75).—Normal blood plasma contains no phosphorised protein, and probably no phosphorus compounds other than phosphatides and inorganic phosphates. The phosphorus of these two classes of compounds certainly comprises more than 97% of all that exists in normal plasma. The precursor in plasma of milk fat and milk phosphorus is of a phosphatide nature. The concentration of calcium in the plasma of cows is quite constant. Small variations can be induced by varying the amount supplied with the rations, but the chief controlling factor is probably the concentration of bicarbonate in the plasma. It is probable that the concentration of calcium tends to vary inversely with that of the bicarbonate. The concentrations of phosphatide and inorganic phosphates in the plasma are highly variable. Both can be made to vary by changing the amount of phosphorus supplied with the rations, though the variations induced in this manner show themselves most markedly in the inorganic phosphate. Both undergo variations as the accompaniment of increasing age and of the later stages of pregnancy. The phosphatide of the plasma shows a marked tendency to rise during the first month of lactation, and to remain high until lactation has ceased. This phenomenon is largely independent of the diet, and is thought to be connected with the fact that near the beginning of lactation there is a tendency for the body fat to be released from its stores and thrown out into the blood.

J. C. D.

**Pyrrole and Melanuria.** PIETRO SACCARDI (*Atti R. Accad. Lincei*, 1919, [v], 28, ii, 85—89).—Administration of pyrrole leads to the formation of melanin in the urine in the case of the rabbit, but not in that of the dog; the latter, being essentially a carnivorous animal, appears easily to oxidise those products of the scission of proteins which lead to the formation of pyrrole, whereas with herbivorous animals the oxidation proceeds only as far as melanogen. Melanins have been obtained from rabbits' urine, from cuttle-fish, from black hair, from the choroid, and from a melanotic tumour.



the properties and reactions of the different products being described. These melanines all resemble closely pyrrole-black obtained by the chemical oxidation of pyrrole; when heated in a test-tube, they yield crystalline sublimates in the form of black, orthorhombic lamellæ, whereas precipitation of the melanines gives amorphous masses.

The glandular oxidation of pyrrole in aqueous suspension containing a few drops of toluene has been studied in vitro at about 40°, the glands used being the mamma, liver, testicles, thyroid, kidneys, and spleen of the ox. The glandular tissue gradually turns brown, and assumes the appearance of an ordinary melanotic tumour; the most intense blackening is shown by the liver and spleen, the testicles, kidneys, and thyroid following in order. The mamma exhibits no blackening after six days, and even undergoes putrefaction, in spite of the presence of toluene. Addition of adrenaline accelerates the blackening of the glandular organs.

T. H. P.

#### **The Physical Theory of the Action of Drugs and Poisons.**

I. TRAUBE (*Biochem. Zeitsch.*, 1919, **98**, 177—197).—A theoretical paper. The pharmacological action of drugs and toxins is attributed mainly to their physical properties. It is urged that more attention ought to be given to the physical side of these principles in the study of chemotherapy.

S. S. Z.

#### **The Biological and Pharmacological Properties of Chlorophyll.**

EMIL BÜRGI and C. F. VON TRACZEWSKI [with (FRL.) SCHEINA BASS, A. BRAUNSTEIN, and (FRL.) S. FRIDKISS] (*Biochem. Zeitsch.*, 1919, **98**, 256—284).—The hæmoglobin-forming capacity of chlorophyll was studied in a series of experiments in which the latter was administered to rabbits made anæmic by means of bleeding and by the action of phenylhydrazine. It was found that chlorophyll, as well as iron, when given in large doses possessed a blood-forming capacity. Both chlorophyll and iron were equally effective, whether the experimental anæmia was induced by bleeding or by the administration of phenylhydrazine. Small doses of chlorophyll were found to possess a "sensitising" effect on the action of iron in the production of blood.

S. S. Z.

#### **Blood-forming Properties of Chlorophyll.**

R. GRIGORIEV (*Biochem. Zeitsch.*, 1919, **98**, 284—294).—Chlorophyll in the form of phæophytin possesses a higher blood-forming capacity than iron when given to normal or naturally anæmic rabbits. The best results are achieved with these animals by the administration of a combination of iron and chlorophyll.

S. S. Z.

#### **Maximum Production of Glutamine by the Human Body as Measured by the Output of Phenylacetylglutamine.**

CARL P. SHERWIN, MAX WOLF, and WILLIAM WOLF (*J. Biol. Chem.*, 1919, **37**, 113—119).—No marked increase in sulphur metabolism

followed the ingestion of phenylacetic acid by man. This does not agree with the experimental results of E. and H. Salkowski working with rabbits (A., 1879, 662). Intestinal putrefaction, as measured by the excretion of ethereal sulphates, is decreased after administration of phenylacetic acid. About half of the acid administered was excreted in combination with glutamine.

J. C. D.

**Comparative Metabolism of certain Aromatic Acids. III. Fate of *p*-Nitrophenylacetic Acid in the Organism of Fowl, Dog, and Man.** CARL P. SHERWIN and MAX HELFAND (*J. Biol. Chem.*, 1919, **40**, 17—27).—The human organism eliminated 68.7% of the ingested *p*-nitrophenylacetic acid in the urine in the unchanged condition. Attention is drawn to the peculiar fact that this acid, although toxic to the body, is excreted without having been rendered innocuous by combination with some substance, such as glycine, in its passage through the tissues. When administered to the dog, the greater part is excreted unchanged, but some is found to be present in the urine as *p*-nitrophenylaceturic acid. In the case of the fowl, a certain amount of the *p*-nitrophenylacetic acid is excreted unchanged, but the greater part is combined with ornithine in the body and excreted as *p*-nitrophenylacetylornithinic acid,  $C_{21}H_{22}O_8N_4$ , short, thick, irregular needles, m. p. 184—185°.

J. C. D.

**Behaviour of Sudan III in the Animal Organism.** B. E. READ (*J. Biol. Chem.*, 1919, **37**, 121—135).—Sudan III dissolved in oil and administered intraperitoneally, subcutaneously, or by the mouth is absorbed, and may be traced in the lymph, blood, and bile. It is transported to the fatty tissue of the body, being deposited particularly in the omentum. It is excreted in the faeces, and is not found in the urine of normal animals. Ordinary commercial preparations of Sudan III contain more or less impurity of a toxic nature. The foreign substances are excreted in the urine, which is deeply coloured, and may cause death. J. C. D.

## Chemistry of Vegetable Physiology and Agriculture.

**The Catalase of Bacteria. II.** MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **92**, 129—139. Compare A., 1918, i, 517).—The bacterial catalase obtained by the author obeys the same reaction laws as catalases already studied.

S. S. Z.

**Acidity Relationships of True Lactic Acid Bacteria.** OLOF SVANBERG (*Medd. K. Vetenskapskad. Nobel-Inst.*, 1919, **5**, No. 2, 1—10).—The author has investigated the acidity conditions

under which various micro-organisms can ferment milk and under which they can continue to grow. The change in the acidity of milk and whey by *Streptococcus lactis* has been ascertained at 16° and 37°, both by titration with *N*/10-sodium hydroxide and by Sørensen's method. At 16°, the  $P_H$  value in both cases is the same, 4.0, but the titration values are very different. *Bacterium casei*  $\epsilon$ , in milk and wort at 35° raises the acidity to  $P_H=3.05$ . If a pure *S. lactis* culture is placed in milk and allowed to act until the maximum acidity is reached, and the acidity is neutralised by alkali, the coccus will again produce acid, but the final concentration will be less than before, and this will be continued if the process of alternate fermentation and neutralisation is continued. The final acidity value is reduced by the addition of sodium lactate to milk proportionally to the lactate concentration. The acid tolerance of *S. lactis* is determined for sulphuric acid, hydrochloric acid, and phosphoric acid, and the same value found in each case, namely,  $P_H=3.4$  at 18°; in the case of *B. casei*  $\epsilon$ , the acid tolerance is found to be  $P_H=3.0$  at 35° for hydrochloric acid and phosphoric acid. The alkali tolerance of *S. lactis* at 18° lies at  $P_H=8$ . J. F. S.

**The Surface Action of the Homologues of Hydroquinine and their Toxins.** I. TRAUBE (*Biochem. Zeitsch.*, 1919, 98, 197—205).—The hydrocupreines and their homologues show a parallelism between their disinfecting power against many bacilli and cocci, mostly gram-positive organisms, and their surface action. An analogy also exists between the susceptibility of bacteria towards basic stains and their power of adsorption of hydrocupreines and their toxins. S. S. Z.

**Gentian-violet, its Selective Bactericidal Action.** M. L. CROSSLEY (*J. Amer. Chem. Soc.*, 1919, 41, 2083—2090).—Gentian-violet is a mixture of dextrin and dye in almost equal proportions. The dye being a mixture consisting chiefly of hexamethylparosaniline hydrochloride and pentamethylparosaniline hydrochloride with small amounts of the tetramethyl compound and lower homologues.

The selective bactericidal action of gentian-violet is no greater than that of its component dyes, and gentian-violet has no advantage over these in selective or differentiating power. Organisms which were gentian-positive were also gram-positive, the structure of the dye and of the organism being important factors in the selective action. The concentration of the dye is an important factor in determining its power to kill an organism. Not one of the dyes examined was effective for *B. subtilis* in dilutions greater than 1 in 100,000. *B. mycoides* was, however, killed by malachite green in dilution of 1 in 100,000, by rosaniline in dilution of 1 in 200,000, and by gentian-violet, or either of its two principal components, in dilution of 1 in 300,000. The basic nitrogen groups appear to be the reactive groups, and their action is intensified by substitution of methyl for amino-hydrogen. W. G.

**The Influence of Potassium Salts on the Enzyme of *Aspergillus Oryzae* which Liquefies Starch.** GEN-ITSU KITA (*Mem. Coll. Eng. Kyoto*, 1918, 2, 1).—Potassium salts promote the property of the enzyme to liquefy starch even when the saccharification is retarded. On the addition of suitable quantities of these salts to the mash no blue coloration is obtained with iodine after the fermented wort is boiled. This reaction, according to the author, is usually present when these salts are not added. The above facts are of technical significance. S. S. Z.

**Formation of Acids by Moulds and Yeasts. II.** FRIEDRICH BOAS and HANS LEBERLE (*Biochem. Zeitsch.*, 1918, 92, 170—188. Compare A., 1919, i, 508).—The formation of acids by *Mycoderma*, *Oidium*, and *Aspergillus niger* in media containing various carbohydrates and nitrogenous ingredients has been studied. The greater part of the acid is formed from the carbohydrate. When, however, an ammonium salt of a strong acid forms the source of nitrogen, the liberated acid suppresses the formation of acid from the carbohydrate. The ammonia formed in the fermentation process from the various nitrogenous compounds by means of enzymic action greatly influences the formation of acid. This is dependent on the character of the organism and the nature of the carbohydrate employed. S. S. Z.

**Natural and Artificial Formation of Glycerol in Alcoholic Fermentation.** CARL NEUBERG and ELSA REINFURTH (*Biochem. Zeitsch.*, 1918, 92, 234—267).—By employing sodium sulphite as "fixing" agent for the acetaldehyde formed in alcoholic fermentation an equivalent amount of glycerol is also formed. More than 70% of the theoretical amount of acetaldehyde is thus fixed. The amount of acetaldehyde and glycerol produced increases with the amount of sulphite employed. Acetaldehyde and glycerol are therefore not only by-products, but are produced in considerable quantities in certain stages of alcoholic fermentation. S. S. Z.

**Autolysis of Yeast in its Dependence on Hydrogen and Hydroxyl-ions.** K. G. DERNBY (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, 3, No. 23, 1—26).—On the basis that enzymes are amphoteric electrolytes, the author has examined the autolysis of yeast at various temperatures in the presence of electrolytes. It is shown that the simple yeast cell contains enzymes which are capable of degrading albuminous substances. These enzymes are analogous in type with those present in specific animal organs. The enzymes identified in the paper are (a) yeast pepsin, which degrades albuminous substances to peptones, and has a maximum activity at  $P_H=4-4.5$ , (b) yeast tryptase, which does not attack the yeast albumin, but destroys gelatin, casein, Witte-peptone, and similar substances, and has a maximum activity at  $P_H=7.0$ , (c) yeast eriptase, which degrades polypeptides to amino-acids and has a maximum activity at  $P_H=7.8$ . The autolysis of yeast is brought about by these enzymes and consists in a successive degradation of

albumin; it can only proceed when the different enzymes can operate simultaneously. The best hydrogen-ion concentration for the process is  $P_H=6.1$ , which lies between that of yeast tryptase and yeast pepsin.

J. F. S.

**Extraction and Concentration of the Water-soluble Vitamins from Brewer's Yeast.**

THOMAS B. OSBORNE and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1919, **40**, 383—394).—By precipitation of a dilute acetic acid extract of yeast with alcohol the authors have succeeded in obtaining a fraction which appears to contain a very large proportion of the water-soluble accessory substance present in the original yeast. The chemical nature of the substances in this fraction is not yet determined.

J. C. D.

**Examination of the Urease-content of Indigenous Seeds.**

D. H. WESTER (*Chem. Weekblad*, 1919, **16**, 1548—1551).—The urease content of a large number of seeds was determined. It varied from nil or very small amounts up to a considerable quantity in the laburnum. Plants of the same natural order differ widely in regard to the urease content of their seeds. In no case did the amount of urease approach that found in soja beans or canavalia beans, and of these the latter contained approximately ten times as much urease as the former.

W. J. W.

**Do Seedlings Reduce Nitrates?**

J. DAVIDSON (*J. Biol. Chem.*, 1919, **37**, 143—148).—The author reaches the conclusion that growing seedlings do not, as part of their metabolic processes, reduce the nitrates in the outside medium in which they are growing.

J. C. D.

**Complex Iron Salts. I.**

OSKAR BAUDISCH (*Biochem. Zeitsch.*, 1918, **92**, 189—198).—In mixed aqueous solutions of ferric chloride and formaldoxime, phloroglucinol, catechol, or resorcinol exposed to the air, trivalent iron is slowly reduced to its bivalent form in the presence of dilute hydrochloric acid. Similarly, in admixed solutions of ferric chloride and quinol, acetylacetone, acetoacetic ester, salicylaldehyde, salicylic acid, and catechol-*o*-carboxylic acid, the above reduction is only effected after exposure to the rays of a mercury quartz lamp or sunlight. Aqueous solutions of ferric chloride and dimethylglyoxime, on the other hand, are not reduced even after exposure to the light. The chemistry of these observations and their bearing on some physiological phenomena of the plant are discussed.

S. S. Z.

**Presence in Plants of Hæmatoid Iron Compounds. III.**

G. GOLLA (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 146—150).—Experiment indicates that the peroxydasic function in plants is due in most cases, not only to true enzymes, but also to various iron compounds. The latter are probably catabolic products of more complex compounds, such as the hæmatoids, which largely form incrustations on the cellular membranes, and are, in virtue of their

physical state, able to act between the oxidisable substances and the peroxides. T. H. P.

**Position and Osmotic Pressure.** O. ARRHENIUS (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 15, 1—20).—A discussion of the relation between the osmotic pressure of the cell sap and the position of plants and trees. By "position" is meant, not only the geographical position, but also the factors, such as light, heat, moisture, winds, composition of the substratum, etc., which affect the growth of the plants. T. S. P.

**The Isoelectric Points of the Proteins in certain Vegetable Juices.** EDWIN J. COHN, JOSEPH GROSS, and OMER C. JOHNSON (*J. Gen. Physiol.*, 1919, 2, 145—160).—The hydrogen-ion concentration of filtered potato juice is approximately  $10^{-7}N$ . The isoelectric point of tuberin, the chief protein of the potato, determined by the cataphoresis method, is at a hydrogen-ion concentration slightly lower than  $10^{-4}N$ . At acidities greater than the isoelectric point, tuberin exists combined with acid. The isoelectric point of the protein in carrot juice coincided with that of tuberin, and the properties of carrot juice and potato juice were found to be remarkably similar.

The protein of the tomato existed in a precipitated form near its isoelectric point. Accordingly, it was not present to any extent in filtered tomato juice. If, however, the considerable acidity of the juice was neutralised, the protein dissolved and was filterable. The addition of sufficient acid to make the hydrogen-ion concentration slightly greater than  $10^{-5}N$  again precipitated the protein at its isoelectric point. J. C. D.

**Fat-soluble Vitamine. II. The Fat-soluble Vitamine Content of Roots, together with some Observations on their Water-soluble Vitamine Content.** H. STEENBOCK and E. G. GROSS [with M. T. SELL] (*J. Biol. Chem.*, 1919, 40, 501—531).—In the plant kingdom, the occurrence of the fat-soluble vitamine cannot always be associated with a preponderance of actively functioning cells, as distinguished from those that serve primarily as storage organs. Thus the sweet potato is rich in this accessory factor, whilst the ordinary potato contains very little; similarly, in the case of the roots, carrots contain much of the vitamine, but beets and mangels do not.

In the case of the water-soluble vitamins, the carrot, rutabaga, and dasheen contain more than do sugar-beets and mangels.

J. C. D.

**Reducing Action of Roots of the Gramineæ: Reduction of Calcium Nitrate. I. and II.** GIOVANNI SANI (*Atti R. Accad. Lincei*, 1919, [v], 28, ii, 199—201, 244—247).—When the roots of wheat, maize, and oats, gathered at the beginning of the flowering period, are pounded in a mortar and then extracted with boiling water, liquids are obtained which exert pronounced reducing action

on Fehling's solution. The pulped roots, which have an acid reaction, are also able, in the cold, to reduce calcium nitrate, this reduction being inhibited by the presence of alkaline Rochelle salt solution. The reduction of calcium nitrate proceeds only to a definite limit, and then ceases entirely, the product of the reduction apparently acting as a poison towards the reducing agent; in the plant itself, however, such poisoning action would not occur, utilisation of the reduction product preventing its accumulation. The nature of this reduction product has not yet been established.

T. H. P.

**Globulin of the Coconut, *Cocos nucifera*. I. Preparation of Coconut Globulin. Distribution of the Basic Nitrogen in Coconut Globulin.** CARL O. JOHNS, A. J. FINES, and C. E. F. GERSDORF (*J. Biol. Chem.*, 1919, **37**, 149—153).—The globulin contains the following amounts of basic amino-acids: cystine, 1.44%; arginine, 15.92%; histidine, 2.42%; lysine, 5.80%. Tryptophan is present. The free amino-nitrogen was found to equal nearly one-half of the lysine nitrogen.

J. C. D.

**Globulins of the Jack Bean, *Canavalia ensiformis*.** JAMES B. SUMNER (*J. Biol. Chem.*, 1919, **37**, 137—142).—Two crystalline globulins and one non-crystalline globulin have been isolated from the jack bean. *Concanavalin B* crystallises in needles, slowly soluble in 10% sodium chloride, soluble in excess of alkali; *concanavalin A* crystallises in bisphenoid form, insoluble in any but concentrated salt solutions; canavalin, the uncrystallisable globulin, is readily soluble in 1% sodium chloride solution (compare Jones and Johns, A., 1917, i, 191).

J. C. D.

**Examination of the Urease-content of Soja Beans from Various Sources.** D. H. WESTER (*Chem. Weekblad*, 1919, 16, 1552—1556).—Nearly all the varieties examined showed a high urease content, and this was not diminished by age. The lowest enzymic action was found in soja beans from the Cameroons and Germany, which raises an interesting question in regard to diminution of effectiveness brought about by transferring the plant from its original habitat, Asia.

W. J. W.

**A Quantitative Relation between Soil and the Soil Solution brought out by Freezing-point Determinations.** BERNARD A. KEEN (*J. Agric. Sci.*, 1919, **9**, 400—415).—Bouyoucos and his co-workers, by determinations *in situ* of the freezing-point depression of soil solution, at varying moisture contents, have shown that the soil solution in quartz sand and extreme types of sandy soil obeys approximately the same law as dilute solutions, but that the soil solutions of ordinary soils do not obey this law (compare *J. Agric. Sci.*, 1914, **6**, 456). Bouyoucos assumes that some of the soil water is rendered unfree in the sense that it does not take part in the depression of the freezing point. The present author, accept-

ing the truth of this assumption, and using some of Bouyoucos's data, has shown that the water rendered unfree is not a constant amount, but varies with the total moisture content. A definite relation exists between the free, unfree, and total moisture expressed by the equations  $Y_n = cM_n^x$  and  $Z_n = Y_n^{1/x}/c^{1/x} - Y_n$ , where  $c$  and  $x$  are constants for any one soil, and  $M_n$ ,  $Y_n$ , and  $Z_n$  represent respectively the total, free, and unfree water. Over the experimental range the ratio of free to total water continually decreases, and that of unfree to total water continually increases as the total moisture diminishes in amount. The constant  $c$  contains an unknown factor, namely, the quantity of free water at the highest amount of total water used in the experiments, and according to the value arbitrarily assigned to it so the amount of unfree water may continually decrease with decrease of total moisture over the experimental range or may increase to a maximum and then decrease. The same general conclusions on the relations existing between the soil and its moisture constant as were drawn from the author's experiments (compare *loc. cit.*) on the evaporation of water from soil, again follow.

W. G.

#### Soil Acidity, the Resultant of Chemical Phenomena.

H. A. NOYES (*J. Ind. Eng. Chem.*, 1919, **11**, 1040—1049).—Chemical reactions are held to be the cause of soil acidity. The presence of free hydrogen ions in the soil extract is considered to be due to hydrolysis. As regards the action of organic matter, physicochemical explanations of the hydrolysis of silicates and of organic matter and the ability of organic matter to form complex ions with bases are more satisfactory than are "adsorption" theories. The reaction of a soil at any time depends on the nature of its constituents and the proportions in which they are present with water. Change in the water content, removal of substances from solution, and the addition of other substances, all alter the reaction of the soil in accord with the law of mass action.

W. P. S.

**The Richness in Copper of Cultivated Soils.** L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1919, **169**, 937—942).—The authors have not estimated the total copper, but the amount which is dissolved when 6 grams of the soil are boiled very gently for half an hour with 50 c.c. of 10% sulphuric acid. Arable soils contain very little copper, the amount varying, in the soils examined, from 1 to 50 mg. per kilogram of soil, but in the case where the high figure was obtained the soil had carried crops which had frequently been treated with copper sulphate. In the case of vineyard soils, where it was known that the vines had been treated with copper sulphate over a long period of years, the copper content rose to as high as 250 mg. per kilo. of soil. The copper was almost entirely found in the surface layer of the soil, the penetration being extremely slow. Despite the high copper content of some of these soils, there was no indication of any toxic effect on the vines.

W. G.



**The Amount and Composition of Rain Falling at Rothamsted (Based on Analyses made by the late Norman H. J. Miller).** E. J. RUSSELL and E. H. RICHARDS (*J. Agric. Sci.*, 1919, 9, 309—337).—A summary of the results of analyses of Rothamsted rain water made by the late N. H. J. Miller from 1888 to 1916. The rain water contained, on an average, 0.405 part per million of ammoniacal nitrogen, 0.204 part per million of nitric nitrogen, 2.43 parts per million of chlorine, and 10 parts per million of dissolved oxygen. Both the yearly and monthly fluctuations of ammoniacal nitrogen move in the same direction as the rainfall, the general level being highest in May, June, July, and August, and lowest in January, February, March, and April. Up to 1910 the nitric nitrogen fluctuated in amount year by year and month by month in the same way as the ammoniacal nitrogen, but since that date there has been no simple relationship. The fluctuations of the chlorine content of the rain closely follow the rainfall, but the general level is much higher during the months September to April than during the summer months.

The sources of ammonia in the rain are given as the sea, the soil, and city pollution; the soil is indicated as an important source by the fact that the ammonia content is high during periods of high biochemical activity in the soil, and low during periods of low biochemical activity. Further, the close relationship between the amounts of ammoniacal and nitric nitrogen suggests either a common origin or the production of nitric compounds from ammonia. It seems probable that the chlorine comes from the sea, but some may come from fuel.

During the period under examination there has been a rise in the amounts of nitric nitrogen and of chlorine in the rain, and a tendency for the ammonia content to drop. It is suggested, as a possible explanation, that some former source of ammonia is now producing nitric nitrogen; it is possible that modern gas-burners and grates tend to the formation of oxides of nitrogen rather than ammonia.

There is a marked difference in composition between summer and winter rain water, which suggests that these may differ in origin. The winter rain resembles Atlantic rain in its high chlorine and low ammonia and nitrate content; the summer rain is characterised by low chlorine but high ammonia and nitrate content, and it is suggested that it may arise by evaporation of water from the soil and condensation at higher altitudes than in the case of winter rain.

W. G.

## General and Physical Chemistry.

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**The Constitution of the Atom and the Properties of Band Spectra.** H. DESLANDRES (*Compt. rend.*, 1919, **169**, 1365—1371. Compare A., 1919, ii, 206, 310, 441, 486).—Further evidence is given in support of the views previously published (*loc. cit.*). The author emphasises the fact that the formula given (A., 1919, ii, 206, 310) is only a first approximation, and offers some explanation of the divergencies found in certain cases. W. G.

**Intensity Relations in the Spectrum of Helium.** T. R. MERTON and J. W. NICHOLSON (*Phil. Trans.*, 1919, **A**, **220**, 137—173).—The spectrum of helium has been examined by photographing the radiation in front of an aluminium cathode in a tube containing helium of such a pressure that the thickness of the dark space was about 1 mm. A number of experiments were made with mixtures of helium and other gases, particularly hydrogen. The most striking phenomenon observed relates to the difference in behaviour between the series of helium and parhelium, for, in the former, lines belonging to a series maintain a practically constant intensity ratio at every point, whilst in the latter the relative intensity of any two lines of the same series varies with the distance from the cathode. In the case of lines belonging to the principal series, the seat of maximum emission is closer to the cathode, and falls away with increasing distance from this point more rapidly than in the case of lines belonging to associated series. The diffuse series appear to preserve the most uniform intensity over a wide range of conditions. J. F. S.

**Spectrum of Neon.** F. PASCHEN (*Ann. Physik*, 1919, [iv], **60**, 405—453).—An account is given of a very complete examination of the spectrum of neon from  $\lambda$  9840.42 to  $\lambda$  2550.55. A long table is given of the wave-lengths, intensities, and the spectrum combination of each line. The regularities between the lines of the principal and subsidiary series are investigated and discussed. J. F. S.

**Emission Spectra and the Chemical Reactions taking place in the Source of Radiation.** ANGEL DEL CAMPO (*Anal. Fis. Quim.*, 1919, **17**, 247—270).—Attention is directed to slight variations in the spectrum of the same element as described by different observers. The author regards these as being due to chemical reactions, notably oxidation and reduction, occurring within the radiant arc. These reactions may be localised, according to circumstances, in the immediate neighbourhood of the electrodes or in the middle of the arc itself, thus giving rise to a "polar effect" in the photograph. This is illustrated in the case of the

silica spectrum, which shows variations as different sections of the arc between the carbon electrodes are examined. The view is expressed that the variations are due to the presence or absence of a reduction product, the suboxide  $\text{SiO}$ . A similar phenomenon is observed with magnesium, and is attributed to the suboxide  $\text{Mg}_2\text{O}$ . In studying the spectra of various specimens of aragonite, three new lines, 2554.6, 2563.8, and 2565.0 A.U., were observed. These were given by all samples of naturally occurring calcium carbonate examined, but not by pure hydroxide. In both cases the oxide formed is reduced to metal in contact with the carbon. This is immediately re-oxidised in the arc, but in the former case the protective action of the carbon dioxide liberated at the same time ensures the persistence of the metallic vapour for a longer time and range, so that the radiation from the metal is rendered perceptible. Further experiments confirmed the view that the lines in question belong to the calcium spectrum, and are not due to impurities in the substances examined.

W. S. M.

**The Emission of Positive Luminous Particles at High Temperatures by the Alkali Metals.** G. A. HEMSALECH

(*Compt. rend.*, 1920, 170, 44—47).—Using the graphite plate with a layer of carborundum, the plate being electrically heated as previously described (compare this vol., ii, 1, 2), it is shown that if the plate is first covered with a thin layer of the chloride, carbonate, or oxide of one of the alkali metals, and this, in turn, covered with carborundum, positively electrified particles are emitted at varying temperatures. All the elements in the alkali group emit positive particles, and for a given temperature the extension and development of the luminous trajectories vary directly with the atomic weights, and in consequence the critical temperature, or temperature at which the phenomenon is apparent, varies inversely with the atomic weight. For lithium the critical temperature is  $2700^\circ$ , and for caesium  $1900^\circ$ . Two hypotheses are put forward to explain this phenomenon, but further work is necessary before a definite explanation can be given.

W. G.

**[The Emission of Positive Luminous Particles at High Temperatures by the Alkali Metals.]** A. DE GRAMONT (*Compt. rend.*, 1920, 170, 47).

—The author states that Hemsalech used a monochromatic, optical pyrometer for the temperature measurements in his work (preceding abstract). The instrument was calibrated and corrected up to  $2500^\circ$ , above which temperature extrapolation was necessary. At  $2700^\circ$  the temperature readings are accurate to  $\pm 50^\circ$ .

W. G.

**The Direct Arc Spectra of Metals with Moderately High Melting Points.** A. DE GRAMONT (*Compt. rend.*, 1920, 170, 31—38).

—A comparison of the direct arc spectra with the spark spectra and the carbon arc spectra in the case of the metals zinc, cadmium, tin, lead, antimony, bismuth, magnesium, and aluminium. By the photographic device employed, the three spectra were obtained in

successive coincidence, thus permitting of a direct comparison of the rays. By this means, it has been possible to detect in the direct ray spectra on the one hand certain rays of the spark spectra, considered by Lockyer as strengthened, and which occur in the direct spectra with a marked intensity, and on the other certain rays of the spark spectra, also classed as strengthened, but which are only fugitive in the direct arc spectra. The latter group of rays appears at the positive pole at the moment of striking the arc. They can most easily be seen by alternately making and breaking the arc. The detailed results are given for each of the metals, and the general conclusions to be drawn are that the arc spectra must not be considered as invariable and always identical. They are subject to considerable variations, not only in the intensities of certain rays, but also in the appearance of the rays, these variations being closely connected with the intensity of the current producing the arc.

W. G.

**New Lines in the Arc Spectrum of Silver between  $\lambda$  4500 and  $\lambda$  2300.** M. A. CATALÁN (*Anal. Fis. Quim.*, 1917, 15, 483—486).—Measurements of eighty new lines were made with wave-lengths corresponding with similar lines in the spark spectrum described by Exner and Haschek ("Tabellen der Funkenlinien," 1902).

W. S. M.

**New Lines in the Arc Spectrum in Air of Iron between 2300 and 1980 Å.U.** S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1917, 15, 434—444).—Measurements of more than 288 new lines in the arc spectrum of iron are given, extending the spectrum from 2300 Å.U. to 1994 Å.U.

W. S. M.

**New Lines in the Arc Spectra of Nickel and Cobalt between 2300 and 2000 Å.U.** S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1918, 16, 338—350).—A total of 66 new lines for nickel and 165 for cobalt in the given range was measured.

W. S. M.

**Photochemistry of Thallous Chloride.** CARL RENZ (*Helv. Chim. Acta*, 1919, 2, 704—717).—The action of light on thallous chloride has been investigated; the action was carried out with the dry substance and with thallous chloride under water, hydrochloric acid, ammonia, ethylamine, ethyl alcohol, glycerol, toluene, xylene, and pyridine. In all cases, a darkening occurs, which passes through the shades greyish-brown, dark greyish-brown, and blackish-brown. The change is due to the formation of a photo-thallous chloride and thallous-thallic chloride. Hydrochloric acid, even in traces, retards the formation of the photo-chloride, and, after prolonged illumination, various yellow, double thallous-thallic chlorides are formed. Nitric acid and sulphuric acid have a similar retarding action on the formation of the photo-chloride. Ammonia, ethylamine, and the above-named organic substances act as sensitizers in the reaction, and many inorganic salts have a photo-

catalytic action. The sensitiveness of thalious chloride to light depends on its method of formation. Thalious chloride precipitated by metal chlorides is more sensitive than that precipitated with hydrochloric acid, even though the acid has been thoroughly washed out.  
J. F. S.

**Diffusion of Radium Emanation in Water.** EVA RAMSTEDT (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 5, 1—14).—The velocity of diffusion of radium emanation in water at 14° has been determined by means of an apparatus containing a number of metal plates immersed in water. The coefficient of diffusion is found to be 0.820 cm. per day, a value which is of the same dimensions (0.985 at 18°) as that recently found by Rona (*A.*, 1917, ii, 286). Calculating from this value, the product  $D\sqrt{m}$  is found to be 12.2, and the molecular diameter of radium emanation  $1.85 \times 10^{-8}$  cm.  
J. F. S.

**Ionisation Potential of Helium.** J. FRANCK and P. KNIPPING (*Physikal. Zeitsch.*, 1919, 20, 481—488).—Using as source of electrons a glowing wire in helium of pressure 1.5 mm., the resonance potential is found to have the value  $20.5 \pm 0.25$  volts, and from this value the ionisation potential is calculated to  $25.3 \pm 0.25$  volts. Experimentally, the ionisation potential of helium is found to be  $25.4 \pm 0.25$  volts, and the resonance potential has the same value as before. The potential necessary for the removal of both electrons from the helium atom is also determined, and the value  $79.5 \pm 0.3$  volts obtained. The present results are in agreement with those of Horton and Davies (*A.*, 1919, ii, 210), and indicate that the helium atom is much less stable than is indicated by the atomic model of Bohr and Landé.  
J. F. S.

**Conductivity. VI. Behaviour of Mixtures of Two Salts containing a Common Ion in Anhydrous Formic Acid Solution.** H. I. SCHLESINGER and F. H. REED (*J. Amer. Chem. Soc.*, 1919, 41, 1921—1934. Compare *A.*, 1919, ii, 91).—The conductivity of potassium formate in anhydrous formic acid solution has been determined at 25° over the range 0.1207*N*—0.3266*N*. The degree of ionisation and the ionisation constant are calculated in each case, and the latter constant has the value 1.090. Similar measurements were also made for sodium formate and lithium formate; these salts have ionisation constants 0.810 and 0.557 respectively. Conductivity measurements were also made for mixed solutions of sodium and potassium formates, lithium and potassium formates, strontium and potassium formates, and strontium and calcium formates, all in anhydrous formic acid and at 25°. A method of calculating from the ionisation constants the degree of ionisation of each of two salts containing a common ion, when the two salts are both present in solution, has been developed for the case in which both salts obey the law of mass action. It is found that in mixtures of sodium and potassium formates, as

well as of lithium and potassium formates, the mass law is obeyed by both of the highly ionised salts present. On the other hand, solutions of mixtures containing, as one or as both of the salts, alkaline earth formates do not conform to the law, although these uni-bivalent salts when in solution alone seem to follow the law over a certain range of concentration. This appears to make it quite certain that whenever the agreement of the salt with the law is an accidental one, solutions of mixtures containing such a salt will not obey the law. Hence it may be definitely concluded that the agreement between the behaviour of the alkali metal formates, in anhydrous formic acid solution, and the demands of the mass law is a real and not an accidental one. When the total concentration of mixed solutions becomes relatively great, deviation from the mass law occurs also in the solutions which contain uni-univalent formates. It has been found that this deviation begins when the concentration of the non-ionised molecules of one of the salts reaches the same value as that at which deviation begins in the solution of that salt by itself. This seems to be independent of the concentration of the other molecular species present, and to indicate that in concentrated solutions it is the non-ionised molecules, and not the ions, which cause deviation from the mass law, or at least the non-ionised molecules cause deviation at lower concentrations than do the ions.

J. F. S.

**Conductivity. VII. Transference Numbers of the Formates of Sodium, Potassium, and Calcium in Anhydrous Formic Acid.**

H. I. SCHLESINGER and E. N. BUNTING (*J. Amer. Chem. Soc.*, 1919, **41**, 1934—1945. Compare preceding abstract).—The transport numbers of solutions of sodium, potassium, and calcium formate in anhydrous formic acid have been determined by the usual method at 25° for a number of concentrations between 0.09*N* and 0.4*N*. The ionic conductivity of the formate ion is calculated to be 51.5, that of sodium ion 14.6, and potassium 17.5. The transport number of the potassium ion changes with concentration. This is tentatively explained on the assumption that the ion is solvated, and a method for calculating the extent of solvation from the transport numbers is suggested. The results indicate that, if the assumptions made in the calculation are correct, each potassium ion is combined with from six to eight molecules of formic acid. The transport numbers obtained for calcium formate do not substantiate the view that calcium formate in formic acid solution ionises either entirely as a uni-univalent salt or entirely as a uni-bivalent salt. It is therefore possible that both methods of ionisation occur.

J. F. S.

**Electric Conductivity of Weakly Ionised Neutral Salts.**

OLOF SVANBERG (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 26, 1—7).—The equivalent conductivity of potassium antimonyl tartrate and cupric acetate has been determined over the range  $N/4$  to  $N/1024$  at temperatures 0—65°. In the case of potassium antimonyl tartrate the equivalent conductivity increases from 64.4 at

$d=4$  to 134.5 at  $d=1024$  at  $25^{\circ}$ ; the more concentrated solutions (up to  $N/32$ ) at all temperatures follow the Ostwald dilution law, but beyond this point the conductivity increases more rapidly than is demanded by any of the formulæ for the extrapolation of the infinity value. There is no evidence that potassium antimonyl tartrate ionises as the potassium salt of antimonyl tartaric acid, and it is also shown that the salt is not greatly hydrolysed in any of the solutions examined. In the case of cupric acetate the equivalent conductivity at  $25^{\circ}$  increases from 10.8 in  $N$ -solutions to 75.3 in  $N/1024$  solutions, which indicates considerable hydrolysis. The equivalent conductivity at infinite dilution has been obtained by extrapolation, and the following values found: potassium antimonyl tartrate,  $0^{\circ}$ ,  $\Delta_{\infty} = 76$ ;  $25^{\circ}$ ,  $\Delta_{\infty} = 154$ ;  $50^{\circ}$ ,  $\Delta_{\infty} = 260$ ;  $65^{\circ}$ ,  $\Delta_{\infty} = 308$ , copper acetate,  $25^{\circ}$ ,  $\Delta_{\infty} = 90$ . J. F. S.

**Relation between the Electrical Phenomenon in Cloud-like, Condensed, Odorous Water Vapours and Smell-intensity.** H. ZWAARDEMAKER and H. ZEEHUISEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 175—178).—Odorous organic substances in dilute aqueous solution when sprayed yield electric charges. It is found on diluting these solutions to such an extent that the electrical phenomena are only just appreciable that the odour is also just appreciable. It is suggested that both these properties depend in a complicated way on (a) the volatility of the substances, and (b) the lowering of the surface tension of the solvent (compare A., 1918, ii, 351). J. F. S.

**Dielectric Constants considered in Connexion with the Theory of Dipolar Molecules.** OSKAR KLEIN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 24, 1—48).—The dielectric constants have been determined for a number of solutions in organic liquids by means of a resonance method. The solutions examined consisted of (1) methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, amyl alcohol, allyl alcohol, benzyl alcohol, acetone and methyl ethyl ketone in benzene; (2) ethyl alcohol, butyl alcohol, and benzyl alcohol in chloroform. It is shown that the resonance method, which is the method used technically for measuring capacity, is well suited to the measurement of dielectric constants. Solutions of the alcohols in benzene or chloroform of the same normality have the same dielectric constant. Thus  $N$ -solutions of alcohols in benzene have a dielectric constant 2.63, in chloroform solution 5.68. Acetone and methyl ethyl ketone have the same value in benzene solution, namely, 3.09. J. J. Thomson's rule that related substances have the same value for  $(\epsilon - 1)M$  holds absolutely for mixtures of the alcohols and water. Some measurements of Pohrt on the dielectric constants of gases are examined, and yield the temperature-coefficient which is demanded by the dipolar theory. The formula of Debye  $(\epsilon - 1)/(\epsilon + 2) \cdot v = A/T + B$  is changed to the form  $(\epsilon - 1)(v - b) = A/T$ , in which for substances which belong to a single group the relationship  $AM = L$  obtains;  $L$  is a constant pro-

portional to the square of the molecular moment, and  $M$  is the molecular weight. These formulæ combine the above-named rules and are in keeping with the dipolar theory. The constant  $L$  has been calculated from several of the experiments, and the values for alcohol (67,000) and acetone (180,000) obtained. The formula  $(\epsilon - 1) = A/T(v - b)$  is applied to the dependence of the dielectric constant on temperature in the case of water, and found to be in keeping with facts. The formula  $K = L/T = M(v - b)(\epsilon_0 - 1) + \mu/[1 + k(\epsilon_0 - 1)]$  holds for infinitely dilute solutions, and together with  $(\epsilon - 1) = A/(v - b)T$  furnishes an exact method for calculating the constants  $K$  and  $b$ . The approximate formula  $K = \mu/[1 + k(\epsilon_0 - 1)]$  is deduced from the above, and allows the determination of  $K$  from a knowledge of the dielectric constant of solutions of the substances concerned.

J. F. S.

**Dielectric Constants of Typical Aliphatic and Aromatic Hydrocarbons, cycloHexane, cycloHexanone, and cycloHexanol.**

THEODORE W. RICHARDS and J. W. SHIPLEY (*J. Amer. Chem. Soc.*, 1919, **41**, 2002—2012).—The dielectric constants of a number of hydrocarbons have been determined at 20°, except in the case of cyclohexanol, which was determined at 25°, by a modified Nernst type of apparatus. The percentage error of the method was much decreased by the use of larger suitably balanced condenser troughs. The following values have been obtained as the mean of several concordant measurements: hexane, 1.876; heptane, 1.973; octane, 1.962; *n*-nonane, 1.967;  $\delta$ -methyloctane, 1.967;  $\beta$ -methyl-octane, 1.967;  $\beta\zeta$ -dimethylheptane, 1.987;  $\beta\delta$ -dimethylheptane, 1.89;  $\beta\epsilon$ -dimethylheptane, 1.89; decane, 1.956; xylene (commercial), 2.375; *m*-xylene, 2.377; ethylbenzene, 2.482; *n*-propylbenzene, 2.364; cumene, 2.400; mesitylene, 2.356; *tert*-butylbenzene, 2.384; cyclohexane, 2.055; cyclohexanone, 18.2; and cyclohexanol, 15.0. The present results are in moderate agreement with the values of previous observers, although in many cases no previous measurement is on record.

J. F. S.

**Relation between the Specific Inductive Capacity of an Electrolyte and the Electric Potential of a Metal placed in it.**

D. L. ULREY (*Physical Rev.*, 1919, **12**, 47—58).—Attention is called to the inadequacy of the Nernst theory of the mechanism of galvanic current production. This theory omits an essential factor, namely, specific inductive capacity of the electrolyte, and employs two hypothetical quantities, metal solution pressure and osmotic pressure of the ions. Transfer of ions between metal and electrolyte is probably brought about by electrical forces, the magnitude of which depends on the specific inductive capacity of the medium. The potential difference between electrodes of the same kind in a two-solution cell was measured for several different percentage mixtures of two liquids for four different cases, and in each case was shown to be strictly proportional to the difference in the specific inductive capacity of the two solutions. The following systems were measured: (a) ethyl alcohol-water (solution of cupric



chloride), with copper electrodes (electrode in the aqueous solution electronegative); (b) ethyl alcohol-water, with calomel electrodes (electrode in the water electropositive); (c) acetone-water, with calomel electrodes (electrode in the water electropositive); (d) methyl alcohol-water, with calomel electrodes (electrode in the water electropositive); and (e) solution of carbamide-water, with platinum electrodes (electrode in the water electropositive). In two cases investigated with copper electrodes, one with platinum electrodes, and six with calomel electrodes, the direction of the *E.M.F.* of the cell is in accordance with the theory that the loss of ions from an electrode is dependent on the specific inductive capacity of the electrolyte rather than on the concentration of those ions in the electrolyte and a solution tension of the electrode. Results obtained further substantiate the theory that the more electropositive metals have the higher specific inductive capacities. CHEMICAL ABSTRACTS.

**Changes of Potential in an Oxidising Agent by Ultra-violet Light.** TORSTEN SWENSSON (*Arkiv. Kem. Min. Geol.*, 1917, 6, No. 12, 1—32).—The effect of ultra-violet light on the potential of solutions of potassium dichromate in sulphuric acid has been examined. The source of light employed was a quartz mercury lamp, and the solutions were maintained at 18° during illumination. The platinum electrode used in the measurements was bright, since it was found that the same value was obtained with both bright and platinised electrodes, but the former reached equilibrium more rapidly. It is shown that during the illumination with ultra-violet light of a solution of potassium dichromate and sulphuric acid, and also during the illumination of either sulphuric acid, potassium dichromate, or chromic acid alone, a change in potential occurs. To achieve this result it is not necessary to illuminate the platinum electrode. In the case of dichromate and sulphuric acid a speedy increase in the potential occurs; whilst when sulphuric acid and dichromate are illuminated separately a decrease in potential occurs. The potential is also decreased for pure chromic acid, and consequently it is shown that the positive effect does not depend on the liberation of this acid on the addition of sulphuric acid to the dichromate. The speedy change in *E.M.F.* is caused by the ultra-violet rays, and is not observed when the action takes place in glass vessels. Both the increase and decrease of *E.M.F.* are of a photochemical nature. Over the range examined the potential change is independent of dilution. The change of potential is in a high degree dependent on the composition of the solution, and shows a maximum at about 75 mol. % potassium dichromate. The decrease in *E.M.F.* after the interruption of the illumination takes place gradually. It is also dependent on the composition, and is most rapid for pure sulphuric acid. It is further greatly dependent on the temperature, and after a moment's boiling the potential becomes normal again. Solutions which have been illuminated, but have returned to their original potential, show on renewed illumination changes in the velocity of the potential

increase and the maximum value. On very bright illumination a rapid increase in *E.M.F.* was observed, which, on interruption of the light, sank very quickly. In this case the illumination of the electrode is essential.

J. F. S.

**Polarisation Tensions of Iron in Solutions of its Complex Salts. Relations between these Tensions and the Dissimulation of Analytical Characters of Ferric Ions.** N. R.

DEAR and G. URBAIN (*Compt. rend.*, 1919, 169, 1395—1397).—The electrolytic cell consists of two half elements joined by a solution of potassium chloride. One half element consists of a metallic electrode in a solution of one of its salts, and the other is an electrode of mercury in a solution of calomel and potassium chloride. The polarisation tension is defined as the difference between the *E.M.F.* of the whole cell and the corresponding value as found in Auerbach's results (compare A., 1912, ii, 123) for the half element containing the mercury electrode. This tension should depend on the number of free metallic ions in the solution, the tension diminishing as the number of ions increases. These measurements should, therefore, in the case of complex salts, give an indication as to how far the metallic constituent of the complex ion is dissimulated. The results obtained with simple and complex iron salts are in agreement with those obtained by Pascal (A., 1909, ii, 487) as to their molecular magnetic susceptibilities.

W. G.

**Hydrogen Overvoltage. II. Applications of its Variation with Pressure to Reduction, Metal Solution, and Deposition.**

D. A. MACINNES and A. W. CONTIERI (*J. Amer. Chem. Soc.*, 1919, 41, 2013—2019. Compare A., 1919, ii, 131).—The increase of hydrogen over-voltage with diminished pressure is shown to follow, in a nearly quantitative manner, from the theory of MacInnes and Adler (*loc. cit.*). The effect of a change in the gaseous pressure on several chemical processes involving the evolution of hydrogen has been studied. The changes in rates of reaction and in reaction efficiencies were found in each case to be in the directions which follow from the change of hydrogen over-voltage with pressure; that is, a decrease of gaseous pressure produces (a) a decrease in the rate of solution of metals in electrolytes, (b) an increase in the efficiency of reductions by metals, and (c) an increased efficiency of metal deposition. The theory explaining the fluctuation of over-voltage accompanying the evolution of a single bubble of hydrogen from a platinum electrode is discussed.

J. F. S.

**Determination of the Hydrogen Exponent.** J. PINKHOF (*Chem. Weekblad*, 1919, 16, 1168—1172).—If, in Poggendorff's method, the normal electrode is replaced by an electrode which does not differ in potential from that of the hydrogen electrode, then, if the composition of the liquid is known and its relation to the potential, the potential of the hydrogen electrode, and therefore the hydrogen exponent, can be determined. The results obtained with a silver electrode in a solution of silver cyanide in

excess of potassium cyanide were not accurate. An electrode of cadmium amalgam in solutions of cadmium salt of various concentrations was found to be suitable. A simple apparatus for the determination is described.

W. J. W.

**Applicability of the Gas Laws to the Strong Electrolytes.** J. N. BRÖNSTED (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 25, 1—19).—A number of solubility and *E.M.F.* measurements have been carried out with the object of testing the hypothesis. "The gas laws hold for ions or salts when other salt solutions are employed as solvents, the concentration of the latter being large when compared with the concentration of the dissolved salt." The *E.M.F.* of cadmium|cadmium sulphate in magnesium sulphate solution has been measured. The element is made up:

Cd | CdSO<sub>4</sub> *c* Mol. | CdSO<sub>4</sub> *c*<sub>1</sub> Mol. | Cd  
(amalgam 3·1%) | MgSO<sub>4</sub> (2 - *c*) mol. | MgSO<sub>4</sub> (2 - *c*<sub>1</sub>) mol. | (amalgam 3·1%)

The value of *c* and *c*<sub>1</sub> varied between 0·1*M* and 1/640*M*, and the temperature was 20° and 39·4°. The potentials obtained are compared with those demanded by the gas laws, and an excellent agreement found. The solubility of dinitrotetra-amminecobalt nitrate, both *α* and *β* varieties, has been determined at 0° and 20° in water, and in solutions of various concentrations of potassium formate, thiocyanate, hydroxide, and nitrate, nitric acid, sodium oxalate, and sodium nitrate. The values obtained are in keeping with the demands of the gas laws.

J. F. S.

**The Electroaffinity of Aluminium. I. The Ionisation and Hydrolysis of Aluminium Chloride. II. The Aluminium Electrode.** JAROSLAV HEYROVSKÝ (*Tl.*, 1920, 117, 11—26, 27—36).

#### Occlusion of Hydrogen and Oxygen by Metal Electrodes.

EDGAR NEWBERY (*J. Amer. Chem. Soc.*, 1919, 41, 1887—1892, 1895—1898); EARLE A. HARDING and DONALD P. SMITH (*ibid.*, 1892—1894, 1897—1898).—Polemical. In the first paper Newbery gives a theoretical discussion of the paper put forward by Harding and Smith (*A.*, 1918, ii, 424), and a criticism of the theory put forward as to the condition of the occluded hydrogen in palladium. The following papers contain replies and counter-replies by Harding and Smith, and Newbery.

J. F. S.

**Electro- and Thermo-chemical Investigation of the Cell Cu or Cu Amalgam | CuSO<sub>4</sub>-Hg<sub>2</sub>SO<sub>4</sub> | Hg.** L. W. ØRØG (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 4, 1—20).—The *E.M.F.* of the elements Cu|*N*-CuSO<sub>4</sub>, Hg<sub>2</sub>SO<sub>4</sub>(sat.)|Hg and Cu(12% amalgam)|*N*-CuSO<sub>4</sub>, Hg<sub>2</sub>SO<sub>4</sub>(sat.)|Hg have been measured at 10°, 15°, 17°, 20°, 25°, and 30° daily for a period of two months. The copper amalgam cells are fairly constant and easily reproducible, and the variation of the *E.M.F.* with temperature is represented by the formula

$$E_t = 0.35030 - 0.00064(t - 20) - 0.0000025(t - 20)^2.$$

The cells with a copper electrode had a slightly higher (0.004—0.006

volt) *E.M.F.* than the amalgam cells, and it is nothing like so constant.  $E_{20} = 0.3542$  and  $dE/dT = -0.00072$  volt. The chemical energy of the copper cell is calculated, and the value  $Q = 24,860$  cal. obtained. The quantity  $Q$  is regarded as made up of three quantities,  $q_1$ ,  $q_2$ , and  $q_3$ ,  $q_1$  being the heat change when 1 gram-atom of copper is withdrawn from the amalgam,  $q_2$  the difference in the heat of formation of copper and mercury sulphate, and  $q_3$  the heat change accompanying the withdrawal of water from the solution by the newly formed copper sulphate. These three values are calculated to  $q_1 = -1297$  Cal. at  $20^\circ$ ,  $q_2 = 7600$  Cal., and  $q_3 = 18.527$  Cal.

J. F. S.

**Passivity of Cobalt.** HORACE G. BYERS and CURTIS W. KING (*J. Amer. Chem. Soc.*, 1919, **41**, 1902—1908).—When cobalt is used as anode in the electrolysis of 0.02*N*-sulphuric acid or sodium sulphate at  $0^\circ$ , it becomes passive if a high current density is employed, but with low current density it remains active; if potassium dichromate is present, it readily assumes the passive condition in all circumstances. The passive state is indicated by an increased drop in potential, a decreased current, by the evolution of oxygen, and by the failure of the cobalt to pass into solution. The potential measurements of a cobalt-platinum cell with various electrolytes, and a comparison with similar results with iron and nickel, show that when the cobalt becomes passive there is a marked increase in voltage across the cell. The potential measurements show that this is due to a change in the potential of cobalt as it changes from the active to the passive condition. Cobalt may therefore be classified with the passive metals, since it exhibits all the characteristics of iron and nickel when they are passive. The essential difference between cobalt and the other passive metals lies in the fact that cobalt, when used as an anode, will not become passive at the low current densities required by nickel and iron. If cobalt has once assumed the passive condition, it will remain so, even though the current density is reduced. In the absence of the anodic relation, cobalt becomes active in acid solution more readily than nickel.

J. F. S.

**Activity Coefficient for Ions.** NIELS BJERRUM (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 16, 1—21).—A theoretical paper in which activity coefficients are considered with the object of bringing strong electrolytes into line with the ionic hypothesis. The *activity coefficient* is defined as the effect of the interionic forces on the activity of the ions, the *conductivity coefficient* as the influence of the interionic forces on the conductivity, and the *osmotic coefficient* as the influence of the interionic forces on the osmotic pressure. Various relationships between these and other similar coefficients are evolved mathematically.

J. F. S.

**Comparative Electrolysis of Various Alkali Chlorides.** E. BRINER, (MLLE.) A. TYKOCINER, and B. ALFIMOFF (*Helv. Chim. Acta*, 1919, **2**, 666—672).—Solutions of the chlorides of sodium,

lithium, and potassium of various concentrations have been electrolysed, and the relative current yields of alkali hydroxide compared. After the passage of 50,000 coulombs through 3·1*N*-solutions of these salts, it is shown that the total current yields are respectively for lithium, sodium, and potassium 75%, 82·5%, and 87%. In the case of lithium chloride, two cases are considered: (*a*) Where the initial concentration of lithium chloride lies on the ascending branch of the conductivity curve (concentrations below 5*N*); here the fraction of the current carried by the lithium chloride diminishes, due to the presence of lithium hydroxide and to the reduction of the salt concentration. (*b*) Where the initial concentration lies on the descending branch of the conductivity curve (concentrated solutions); here the yield is diminished by the lithium hydroxide present, but it is increased by the fact that the reduction of the lithium chloride concentration brings with it an improvement of the conductivity of the salt. J. F. S.

**The Transport Number of the Ions of Cadmium Iodide.**

GEORGES HEYM (*Ann. Physique*, 1919, [ix], **12**, 443—454).—From a series of measurements, it is shown that the transport number of iodine ions varies from 0·55 to 1·0 for solutions of cadmium iodide in which the concentration varies from 0·007 to 0·07 gram of iodine per litre. W. G.

**Electrochemistry of Uranium and the Single Potentials of Some Oxides of Uranium.**

CHESTER A. PIERLÉ (*J. Physical Chem.*, 1919, **23**, 517—553).—The electrolysis of uranium compounds in various solvents and under many conditions has been investigated. It is shown that in aqueous solutions with low current density, uranyl salts deposit, in the first place, hydrated uranic oxide,  $\text{UO}_2 \cdot \text{H}_2\text{O}$ , which is changed as the electrolysis proceeds to a black oxide of varying composition. With higher current density, uranyl sulphate is reduced to uranous sulphate, but in the presence of free acid the deposit obtained is small in amount and poorly adherent, although metallic in appearance. In neutral or alkaline solutions, the deposit formed is a mixture of black and yellow oxides. The use of a porous cup diaphragm does not change the character of the deposits. The deposit obtained when alkaline uranyl tartrate or citrate solutions are electrolysed is an oxide much richer in uranium than that deposited from solutions acidified with tartaric or citric acid. The conductivity of non-aqueous solutions of uranyl salts is a function of the water present, and the deposits formed are oxides contaminated with organic matter. Anhydrous pyridine dissolves anhydrous uranium tetrachloride to form conducting solutions; these, on electrolysis, deposit a compound containing uranium and pyridine on the cathode. Solutions of uranium tetrachloride in acetone do not yield metallic uranium on electrolysis; the solution is a good conductor of electricity. The deposit obtained replaces mercury from mercurous sulphate. Uranium tetrachloride reacts with anhydrous acetone, forming  $\beta\beta$ -dichloropropane. During electro-

lysis, hydrogen is evolved. Solutions of potassium uranyl fluoride, whether acid, alkaline, or neutral, form a deposit containing fluorine; in acid solution, the deposit is  $\text{UF}_4 \cdot 6\text{H}_2\text{O}$ ; neutral and alkaline solutions give a deposit containing uranium tetrafluoride and uranium oxide. Deposits obtained from neutral solutions of potassium uranyl cyanide consist of pure potassium uranate. When acidified with hydrocyanic acid, the deposit is the yellow, hydrated oxide contaminated with a little of the black oxide. The single potentials of the metal and the oxides have been measured by pasting the finely powdered material on a platinum electrode with gelatin. The following potentials of the more stable oxides have been obtained:  $\text{U}_3\text{O}_8 | \text{UO}_2(\text{NO}_3)_{\frac{1}{2}}$ , 14.3 grams per litre  $\| = 0.776$  volt;  $\text{UO}_3 \cdot \text{H}_2\text{O} | \text{UO}_2(\text{NO}_3)_{\frac{1}{2}} \| = -0.860$ ; black oxide from aqueous uranyl salts  $| \text{UO}_2(\text{NO}_3)_{\frac{1}{2}} \| = -0.6872$  volt; uranium 91.49%  $| \text{UO}_2(\text{NO}_3)_{\frac{1}{2}} \| = -0.093$  volt. Uranous oxide,  $\text{UO}_2$ , gives a single potential identical with that obtained for the green oxide,  $\text{U}_3\text{O}_8$ . The black deposit formed when uranium salts are electrolysed is not  $\text{U}_3\text{O}_8 \cdot 2\text{H}_2\text{O}$ , as stated by Smith (*Amer. Chem. J.*, 1879, 1, 329), but a compound,  $\text{U}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ , and it has a different potential to that of  $\text{U}_3\text{O}_8$ .

J. F. S.

**Johan Gadolin's Electrochemical Theory, its Origin and Development.** H. G. SÖDERBAUM (*Medd. K. Vetenskapsakad. Nobelinst.*, 1919, 5, No. 9, 1—14).—Historical.

T. S. P.

**Diamagnetic Phenomenon in Luminous Nitrogen and the Magnetic Behaviour of its Band Spectrum.** W. STEUBING (*Physikal. Zeitsch.*, 1919, 20, 512—519).—The intensity changes of the nitrogen bands in a magnetic field have been examined with the magnet in various positions. It is found that if a flat bulb 33 mm. in diameter is blown in the middle of the tube and the tube filled as for an ordinary spectrum observation, the light passes across the bulb in the ordinary way, except that the positive column is slightly broadened. When the field is made active the middle of the bulb is filled with a blue, luminous sheath, which extends up to the walls and is at right angles to the lines of force of the field. This sheath has an identical spectrum with the negative luminescence, and is probably to be accounted for by the diamagnetic molecules setting themselves at right angles to the magnetic lines.

J. F. S.

**Magnetic Properties of some Rare Earth Oxides at Low Temperatures.** E. H. WILLIAMS (*Chem. News*, 1919, 119, 287—288).—The magnetic susceptibility of the oxides of dysprosium, erbium, gadolinium, samarium, neodymium, lanthanum, and yttrium has been determined at a series of temperatures from  $20^\circ$  to  $-140^\circ$ . The following values are given: Dysprosium oxide,  $20^\circ$ ,  $\chi \times 10^6$ , 233.3°;  $0^\circ$ , 250.0;  $-40^\circ$ , 291.3°;  $-80^\circ$ , 347.4;  $-100^\circ$ , 384.2;  $-120^\circ$ , 430.2;  $-140^\circ$ , 490.0. Erbium oxide,  $20^\circ$ , 188.6;  $0^\circ$ , 201.7;  $-40^\circ$ , 234.8;  $-80^\circ$ , 282.3;  $-100^\circ$ , 314.8;  $-120^\circ$ , 355.0;  $-140^\circ$ , 402.8. Gadolinium oxide,  $20^\circ$ , 129.7;  $0^\circ$ , 138.2;  $-40^\circ$ , 160.7;  $-80^\circ$ , 194.2;  $-100^\circ$ , 217.0;  $-120^\circ$ , 244.6;  $-140^\circ$ , 279.0.

In all cases the oxides were purer than 99.5%. In the case of samarium oxide the susceptibility at  $-140^{\circ}$  was about 10% larger than at  $20^{\circ}$ . Yttrium oxide increases in susceptibility with decrease in temperature, but very slightly, and since the susceptibility is less than  $1 \times 10^{-6}$  the experimental error is relatively large. It is shown that the product of the susceptibility and the absolute temperature is not constant, but decreases with falling temperature to a slight extent. J. F. S.

**The Paramagnetism of Solid Salts and the Theory of the Magnetron.** B. CABRERA (*Anal. Fis. Quim.*, 1918, 16, 436—449).—A mathematical discussion of the Curie-Langevin law when the mutual actions of the paramagnetic atoms are no longer negligible. W. S. M.

**Furnace Temperature Regulator.** WALTER P. WHITE and LEASON H. ADAMS (*Physical Rev.*, 1919, 14, 44—48).—By making the heating coil of an electric furnace one arm of a Wheatstone bridge, and combining this with a galvanometer regulator, thus keeping the resistance of the coil constant, the temperature of electric furnaces may be kept constant. This device is effective regardless of variations in the current supply, and requires no attention, particularly in the case of furnaces which are not directly influenced by the temperature of the room or where the surrounding air is kept constant. The arrangement operates as follows: Changes in the temperature of the furnace, and consequently in the resistance of the heating coil, operate a boom which either hits or misses a contact-maker which controls a suitable relay. This relay operates a larger magnet, which controls the main current. The power available in this regulator is very large; nothing has to be inserted into the furnace cavity, and the lag is practically non-existent. The regulator is often almost at its best under conditions most unfavourable to other regulators. Using this regulator, the authors have kept a small furnace constant to within  $0.1^{\circ}$  for hours at temperatures from  $500^{\circ}$  to  $1400^{\circ}$ . J. F. S.

**An Analysis of the Radiation Emitted in Gaseous Explosions.** W. T. DAVID (*Phil. Mag.*, 1920, vi, 39, 84—95).—In explosions of coal-gas and air, and of hydrogen and air, the ratio of the energy in the  $2.8 \mu$  radiation emitted to that in the radiation of longer wave-length decreases as the temperature decreases. In the neighbourhood of  $1200^{\circ}$  abs. the  $2.8 \mu$  radiation decreases very rapidly with the temperature, and is negligible at  $1000^{\circ}$  abs. Radiation of longer wave-length is emitted after the temperature has fallen to  $900^{\circ}$  abs., but at this temperature the emission is small. The ratio of the energies in the  $2.8 \mu$  and the  $4.4 \mu$  radiation in coal-gas and air mixtures appears to depend on the composition of the mixture and the temperature. The loss of heat by radiation expressed as a percentage of the heat of combustion of hydrogen and air mixtures, between the limits of composition of 10 and 25.4% of combustible gas, decreases very rapidly as the latter increases.

The variation for mixtures of coal-gas and air between 9.8 and 15% is small. The author attempts a theoretical explanation of these results on the following lines. The intra-molecular energy acquired on combustion by the freshly-formed molecules of carbon dioxide and water is not equally partitioned over the various internal degrees of freedom of the molecules. When the combustion is gentle the intra-molecular energy is concentrated in the rotational degrees of freedom, and in such very low frequency vibrations as the molecules may be capable of executing. As the combustion becomes more violent the higher frequency vibrations share in this energy, and it is possible that during combustion of extreme violence equipartitioning of energy amongst all the internal degrees of freedom of the molecules may be approached momentarily. This is believed to be capable of explaining many phenomena of explosive combustion, such as the pre-pressure period.

J. R. P.

**Isothermals of Monatomic Substances and their Binary Mixtures. XX. Isothermals of Neon from 20° to -217°.**

C. A. CROMMELIN, J. PALACIOS MARTINEZ, and H. KAMMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 108—118. Compare A., 1917, ii, 407; 1918, ii, 9).—The isothermals of neon have been determined over the range 20° to -217° up to a pressure of 90 atms. by the method previously described. From the results of the experiments the authors have calculated the virial-coefficients from the equation of state. It is shown that the  $pv_A$  values obtained in the present work agree in a very satisfactory manner with the older measurements. Only in the isothermal -217.52° is any marked divergence visible, and here the divergence does not exceed 0.5%, whilst for the isothermal -200.08° they do not reach 0.1%.

J. F. S.

**A New Improvement of the Equation of State of Fluids.**

E. ARIÈS (*Compt. rend.*, 1919, **169**, 1140—1143).—A mathematical discussion of the subject.

W. G.

**Equation of Condition.** FRED. G. EDWARDS (*Chem. News*, 1920, **120**, 4—5).—Using Nernst's value in the equation for the mean molecular heat of gases,  $Cv = a + bt$ , it is shown that these linear equations are chords to the curve  $m^2 = k \log T$ , where  $m = 5.95/y$  or  $4 - (2y/2.975)$  below or above  $y = 2.975$ , from which is obtained the general equation  $m^2 = k/\log T = 1/v \log T$ , and hence  $pv = m^2 T$ ,  $m^2$  being a constant for monatomic gases.

W. G.

**Corrected van der Waals's Equation of Condition for the Quasi-diminution of the Molecule.**

E. A. HOLM (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 27, 1—33).—In the corrected van der Waals's equation an infinite series of  $b/v$  appears as the correction factor of the volume. This has been inserted by Boltzmann in an approximated form as  $1 - b/v + 0.375b^2/v^2 - 0.0369b^3/v^3$ . This cannot be true for very small volumes. The equation has been tested on Amagat's oxygen isotherms, and it is



found to be strictly applicable at pressures 250, 300, and 450 atm. and at temperatures  $0^{\circ}$ ,  $15.63^{\circ}$ ,  $99.50^{\circ}$ , and  $199.5^{\circ}$ . The negative divergence found for very high pressures is due entirely to the mathematical incompleteness of the formula. J. F. S.

**Determination of Chemical Constants.** ALFRED C. EGERTON (*Phil. Mag.*, 1920, [vi], **39**, 1—20).—The author emphasises the fact that the usual formula for the calculation of chemical constants from vapour pressures, due to Nernst, cannot give results having any theoretical significance, because the assumptions as to the specific heats at low temperatures which are contained in it have been shown to be incorrect by recent experiments. He therefore modifies the formula by substituting for these assumptions the more exact expressions for the specific heats of solids at low temperatures, and assumes that the atomic heats of gases remain constant and equal to  $5/2 \cdot R$  at the lowest temperatures. The values of the chemical constants calculated by the new formula agree, within the limits of experimental error, with those given by the formula  $-C_0 = C - 1.5 \log M$ , where  $C_0$  is a universal constant, and  $M$  is the atomic weight. The values of  $C$  obtained from the vapour-pressure formula are given in the second column below; those from the above formula in the third column:

	$C$ from vap. press.	$C$ from formula.
Mercury .....	$1.820 \pm 0.032$	1.845
Cadmium .....	$1.65 \pm 0.31$	1.468
Zinc .....	$1.23 \pm 0.26$	1.115

The value of  $C_0$  is found to be  $-1.622$ . The latent heats of vaporisation are calculated from an expression previously used (*Phil. Mag.*, 1917, [vi], **33**, 193), and found to agree with the experimental values, as well as those calculated by the equation  $\lambda = T_0 8.5 \log T_0$  due to Nernst. The value of Stefan's constant  $\sigma$  is calculated, and found to be  $5.27 \cdot 10^{-5}$  erg. cm.<sup>-2</sup> deg.<sup>-4</sup>, which agrees with the value adopted by Planck, but is distinctly lower than the more recently determined values. J. R. P.

**Significance of the Chemical Constant and its Relation to the Behaviour of Gases at Low Temperatures.** F. A. LINDEMANN (*Phil. Mag.*, 1920, [vi], **39**, 21—25).—It is shown that the chemical constant has the dimensions of the logarithm of a pressure if the atomic heat of a monatomic gas becomes zero at the absolute zero. In this case it should be of the form  $K + 3/2 \cdot \log A + 5/2 \cdot \log \theta$ , where  $\theta$  is a characteristic constant of the substance. If the atomic heat of a monatomic gas remains  $5/2 \cdot R$  down to the absolute zero, the chemical constant has the dimensions of a pressure divided by a temperature to the power  $5/2$ , and is of the form  $K + 3/2 \cdot \log A$ . Experimental determinations show that the latter form is true within the limits of error. It follows either that  $\theta$  is very nearly equal to  $1^{\circ}$  for all substances, which seems improbable, or that the atomic heat remains constant down to the lowest temperatures. It is further shown that the chemical constant may be eliminated and the vapour pressure expressed in terms of the pressure of full radiation. It is therefore suggested that the

chemical constant may express the interaction of matter and full radiation rather than requiring that a gas can assume only a finite number of microphases, from the point of view of statistical mechanics, at a given temperature, pressure, and volume. If the value of the chemical constant could, as suggested, be derived from the radiation pressure, the quantum assumption would be avoided in the case of gases, although it would be necessary for the deduction of the law of full radiation.

J. R. P.

**Latent Heat and Surface Energy. II.** D. L. HAMMICK (*Phil. Mag.*, 1920, [vi], **39**, 32–46. Compare A., 1919, ii, 389).—On the assumption that van der Waals's constant,  $a$ , varies with the temperature, a relation is derived between the surface energy  $\rho$ , the molecular volume  $V$ , and  $a_T$ , namely,  $a_T = 6\rho V/d$ , where  $d$  is the molecular diameter. This is valid at low temperatures only. By assuming that  $a_T$  diminishes linearly with the temperature to the critical value,  $a_c$ , latent heats are calculated by Bakker's formula,  $\lambda = a_T(1/v_1 - 1/v_2)$ , for several liquids. The results are in good agreement with experimental values. The ratio  $a_T/a_c$  is found to be the same for many liquids at the boiling point, and equal to 1.4. This leads to the value of Trouton's constant. The empirical relationship between latent heat and surface energy, due to Walden, and the Eötvös-Ramsay law, can also be deduced.

J. R. P.

**Heats of Fusion, Velocities of Crystallisation, and Chemical Affinities in Crystals.** M. PADOA (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 239–243. Compare A., 1919, ii, 51, 96).

—From the considerations previously developed, the conclusion is drawn that the affinity acting in the process of crystallisation should be expressed by, or at least included in, the heat of fusion of the compound, so that, under similar conditions as to molecular magnitude and structure, those compounds exhibiting the greatest velocities of crystallisation should also have the highest heats of fusion.

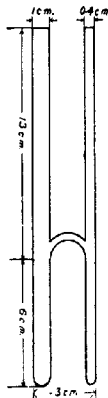
The melting points, heats of fusion, and velocities of crystallisation are tabulated for a number of pairs of isomorphous organic compounds, such as naphthalene and dihydronaphthalene, benzene and cyclohexane, etc. In each pair, the greater heat of fusion corresponds with the greater velocity of crystallisation characteristic of the compound containing double linkings. Further, unsaturated compounds, in general, melt at higher temperatures than the corresponding saturated compounds, this indicating the greater stability of the crystals of the former. As regards heats of fusion, the values for different series of compounds cannot be compared, the value for the saturated ethyl succinate, for instance, exceeding that for benzene; thus, the heat of fusion may be the resultant of various thermal effects, and not merely the effect of the affinity inherent to the union of the molecules in the crystal, in the same way as the heat of solution represents the algebraic sum of the various heats of ionisation, hydration, etc.

With a compound containing a triple linking, such as tolane, the velocity of crystallisation is less than that for the corresponding

isomorphous compound with a double linking (stilbene), and approaches that for the corresponding compound with a single linking (dibenzyl). The parallelism between velocity of crystallisation and heat of fusion is maintained also in this case; the melting points of compounds with triple linkings are likewise lower than those of the compounds with double linkings.

The high velocities of crystallisation shown by compounds with double linkings are explainable on the assumption that change of form on crystallisation is unnecessary with these compounds, which in the liquid state are wholly of the fumaric or wholly of the maleic type, and with the help of the latent valencies crystallise with great rapidity; on the other hand, the compounds with single or triple linkings undergo, in part at least, a preliminary transposition, which results in retardation of the crystallisation. As an instance of the influence of the molecular configuration, it may be noted that the velocity of crystallisation of dibenzyl, with which equilibrium, between the *cis*- and *trans*-forms is possible in solution, is 580 mm. per minute, whereas that of dihydrophenanthrene, which differs from dibenzyl only in the closure of the third ring, and with which no equilibrium between isomeric forms is possible, is 1200 mm. per minute.

It may be, however, that the results obtained with compounds containing the three different linkings are to be explained by the assumption that the latent valencies of the triple linking exert no action in the formation of crystals. Thomsen's thermochemical calculations ("Thermochemische Untersuchungen," 1906, 310) show that the thermal value of a simple linking in the lower members of the paraffin series is 14.71 cal., whereas that of the double linking in the corresponding olefines is 13.27 cal., and that of the triple linking in acetylene, etc., approaches zero. T. H. P.



#### Apparatus for Determining the Melting Point of Very Hygroscopic Substances. H. J. BACKER (*Chem. Weekblad*, 1919, 16, 1564—1565).—

The apparatus consists of a narrow, thin-walled glass tube, into which the material under examination is placed, the tube being then drawn out and sealed. It communicates by means of a small, curved, lateral branch with a wider tube, in which is placed about 2 c.c. of phosphoric oxide, after which this tube is drawn out into a capillary, exhausted by means of a water-pump, and sealed. The material is thus contained in a vacuum desiccator during the determination of its melting point. W. J. W.

**Freezing-point Lowerings in Mixtures of Two Electrolytes.** K. G. DERNBY (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, 3, No. 18, 1—10).—The depression of the freezing point has been determined for aqueous solutions of mixtures of two electrolytes. The following pairs were examined: hydrochloric acid and the

chlorides of sodium, potassium, and magnesium respectively, potassium and magnesium chloride, nitric acid with potassium and magnesium nitrates respectively. The concentrations examined varied between  $0N$  and  $0.8N$ . It is shown that the freezing-point lowerings of mixtures of electrolytes with a common negative ion are always greater than the sum of the individual lowerings. For mixtures of binary electrolytes, such as  $KCl, HCl, NaCl, HCl, KNO_3, HNO_3$ , the lowering of the freezing point is approximately proportional to the concentration of the salt and of the acid. For mixtures of a ternary electrolyte and a binary electrolyte, such as  $MgCl_2, HCl, MgCl_2, KCl$ , and  $Mg(NO_3)_2, HNO_3$ , the lowering of the freezing point increases faster than the concentration. Mixtures of magnesium chloride and hydrochloric acid lower the freezing point more than mixtures of potassium chloride and magnesium chloride of the same concentration.

J. F. S.

**Calculation of the Neutral Salt Action from the Depression of the Freezing Point of Aqueous Solutions.**

SVANTE ARRHENIUS and ERIK ANDERSSON (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, 3, No. 25, 1-9).—A theoretical paper in which, on the basis of the Arrhenius hypothesis of the mechanism of neutral salt action, an attempt is made to calculate the neutral salt action from freezing-point depressions. The osmotic pressure of a solution is strongly influenced by other substances, particularly salts; this is also true of the osmotic pressure of hydrogen ions. Since the velocity of reaction is proportional to the osmotic pressure of the surrounding substance (sucrose or ethyl acetate), and, further, the osmotic pressure of the catalyst (hydrogen ions) increases proportionally, the neutral salt action can be calculated as soon as the corresponding changes of the two osmotic pressures are known. These for the case under investigation are known from the freezing-point measurements of Dernby (preceding abstract) and from the hydrogen-ion activity determinations of Harned (A., 1916, ii, 8). The calculation shows that the method is one capable of furnishing the desired result.

J. F. S.

**Simplification of the Inverse-rate Method for Thermal Analysis.**

P. D. MERICA (*Bull. Bureau Standards*, 1919, No. 336, 101-104).—In plotting and recording cooling curves, the author recommends the following method, using a thermocouple, a direct-reading potentiometer and galvanometer, and two stop-watches. The watches are mounted in a single frame and held in one hand; the potentiometer is set at the desired point. When the time-temperature readings are being made, the stem of both watches is pressed at the moment the galvanometer reaches the zero, thus stopping one watch and so recording the time interval, and starting the other watch on the next interval, which is recorded in the same way. This method saves the time necessary in plotting and reading chronograph records, and does away with the use of expensive chronographs. Specimen curves for the cooling of iron made by this method are given in the paper.

J. F. S.

**Exact Formula for the Saturation Tension of Water Vapour between 0° and 50°.** PAUL SCHREIBER (*Physikal. Zeitsch.*, 1919, 20, 521—523).—The author gives the following formulae for calculating the saturation tension of water vapour at temperatures between 0° and 50°:  $\log s = \log s_1 + \log f(T)$ , in which  $\log s_1 = p + q \log T$  and  $\log f(T)$  is a correcting factor,  $s$  is the corrected saturation tension. The values calculated by this equation are practically identical with the values given in the international meteorological tables. The values  $\log s_1 = -7.0814 + 17.8 \log (10^{-2}T)$ ,  $\log f(T) = 0.0115 - 0.0000494(T - 298)^2$  and  $\log s = -7.0699 + 17.8 \log (10^{-2}T) - 0.0000494(T - 298)^2$  are used in the calculations. J. F. S.

**Boiling Point of Liquids.** F. P. SOEBEL (*Science*, 1919, 50, 49—50).—Assuming that at the b. p. the energy of vibration of the individual molecules of a liquid and of its vapour must be equal, the author deduces the equation  $T_x = mp_x v_x / 1.49$  for a pure liquid, where  $m$  is the molecular weight and  $p_x$  and  $v_x$  the pressure and the volume of the vapour at the absolute b. p.,  $T_x$ . For ordinary liquids containing impurities, the equation becomes  $T_x = (p_x v_x - C)m / 1.49$ , where  $C$  is a constant characteristic of each liquid. In the case of water ( $m = 18$ ;  $C = 8.7$ ), the calculated values of  $T_x$  at 273°, 313°, and 473° (abs.) are 270°, 313.3°, and 473.5° respectively. Similar agreement is found in the case of other liquids in which association does not occur. CHEMICAL ABSTRACTS.

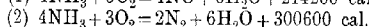
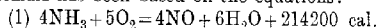
**Vapour Pressure and Free Energies of the Hydrogen Haloids in Aqueous Solution. The Free Energy of Formation of Hydrogen Chloride.** STUART J. BATES and H. DARWIN KIRSCHMAN (*J. Amer. Chem. Soc.*, 1919, 41, 1991—2001).—Determinations have been made of the vapour pressures of hydrogen chloride, hydrogen bromide, and hydrogen iodide above their aqueous solutions between the concentrations 3.2 and 10.0*N*, 5.8 and 11.0*N*, and 6.0 and 9.7*N*, respectively, at 25°, and of hydrogen chloride between 5.5 and 9.2*N* at 30°. By the method employed, which consisted in determining the hydrogen haloid contained in a given quantity of air or nitrogen in equilibrium with its solution, and comparing this with the amount of aqueous vapour which the same air contained when in equilibrium with pure water at the same temperature, partial pressures as small as 0.001 mm. were determined with an accuracy of a few per cent. The vapour-pressure measurements of hydrochloric acid solutions between 3.2*N* and 7.15*N* are in good agreement with the *E.M.F.* data for hydrochloric acid concentration cells. The free energy of formation of hydrogen chloride at 25° is -22,700 cal. The free energies of formation of the halogen acids at various concentrations, 0.1—11.0 mols. per litre, in aqueous solution are given in a table in the paper. J. F. S.

**Constant Temperature Still-head for Light Oil Fractionation.** FREDERICK M. WASHBURN (*J. Ind. Eng. Chem.*, 1920, 12, 73—77).—The apparatus described consists of two essential

parts, namely, a Hempel column and a constant temperature still-head of the type suggested by F. A. Brown (T., 1880, **37**, 49). This still-head is a spiral of about 6 inches diameter made from 12 feet of  $\frac{3}{8}$  inch iron tube; it is surrounded by an oil-bath, which is provided with a stirrer and maintained at the required temperature by a coil of resistance wire, thermo-regulator, relay, etc. The lower end of the spiral is connected with the side-tube of the Hempel column, whilst the upper end is fitted with a thermometer pocket and a side-tube leading to an ordinary condenser. W. P. S.

**Heat of Formation Calculated from the Wave-length of Absorption Bands.** A. L. BERNOULLI (*Helv. Chim. Acta*, 1919, **2**, 720–728).—The author has deduced an expression, whereby from the absorption bands corresponding with characteristic ultra-violet electron vibrations the heat of formation of a compound from its elements may be calculated. This expression for a binary compound has the form  $Q = 0.01128[(\sqrt{\Theta_1/\alpha v_1^2} - \sqrt{\Theta_2/\beta v_2^2}) - \sqrt{\Theta'}/(\alpha + \beta - \delta)v'^2]$ , in which  $Q$  is the heat of formation,  $v_1$ ,  $v_2$ , and  $v'$  the atomic volumes of the constituent elements and the molecular volume of the compound respectively;  $\Theta_1$ ,  $\Theta_2$ , and  $\Theta'$  are the melting points, in absolute degrees, of the elements and the compound respectively,  $\alpha$  and  $\beta$  are the electron numbers or valencies of the elements, and  $\delta$  is the number of charges given up in the formation of the molecule. This formula is tested in the case of a number of binary compounds, and the results compared with the experimental values. The two sets of results are remarkably close; for example, carbon dioxide, calc. 108.3, obs. 106.0; silver chloride, calc. 29.05, obs. 29.0. J. F. S.

**Heat of Reaction of Ammonia Oxidation.** GUY B. TAYLOR (*J. Ind. Eng. Chem.*, 1919, **11**, 1121–1123).—The temperature most favourable to the catalytic oxidation of ammonia by means of air is 800°. In order to determine the amount of external energy required to maintain the catalyst at the optimum temperature a formula has been based on the equations:



The temperature rise is expressed by the formula  $t = Q/C$ , where  $Q$  represents the heat of reaction in calories, and  $C$  the specific heat of the products of the reaction. From 0° to 800° water-vapour is the only gaseous product with an appreciable temperature-coefficient, and this may be taken as 8.34. In the following formula,  $t^0 = (75150x - 21600y)/(7.08 + 3.41x - 0.25y + 8.34V/B - \bar{V})$ ,  $V$  represents the partial pressure of water-vapour,  $B$  the total pressure of the air-ammonia-water vapour mixture,  $x$  the molecular fraction of ammonia in the mixture, and  $y$  the molecular fraction of nitric oxide produced in the oxidation. For maintaining the catalyst at the right temperature, pre-heating the mixture, electric heating, or enriching the current of ammonia and air with oxygen have been shown to give equally satisfactory results. C. A. M.

**Critical Densities of Hydrogen, Helium, and Neon.** J. J. VAN LAAR (*Chem. Weekblad*, 1919, **16**, 1557—1564).—In the cases of hydrogen and helium the extrapolated values for  $D_c$  obtained from the curve  $\frac{1}{2}(D_1 + D_2) = f(T)$  are found to be too high. Thus the figure 0.0310 so obtained for hydrogen would correspond to  $\gamma = 0.46$ , which is an impossible value. The author calculates that for hydrogen  $D_c = 0.0287$ , and for helium  $D_c = 0.0598$  instead of 0.066 as given by the curve.

In the case of neon there is agreement between the extrapolated value and the calculated figure,  $D_c$  being 0.456. W. J. W.

**The "Density Numbers" of Groshans.** W. P. JORISSEN (*Chem. Weekblad*, 1917, **14**, 1066—1071).—The volume in c.c. of 1 gram of a vaporised substance at the boiling point is given by the expression  $82T_{b.p.}/M$ , where  $M$  is the molecular weight. Elimination of  $T_{b.p.}$  between this expression and the boiling point formula of Groshans,  $T_{b.p.} = 27.8M\sqrt{x}/n$ , gives the vapour volume in c.c. of 1 gram  $2280\sqrt{x}/n$ .  $x$  is a constant for the class of substances considered, and  $n$  is the sum of the density numbers of the elements involved (*Ann. Phys. Chem.*, 1849, **78**, 116). For the elements carbon, hydrogen, and oxygen the density numbers are unity, and  $n$  is therefore the number of atoms in the molecule. For other elements  $n$  is greater than unity. For unassociated liquids the expansion in the transition from liquid to vapour is  $570\sqrt{x}$ . By comparing this formula with the expansion determined experimentally by Masson (A., 1891, 379) for methyl, ethyl, propyl, phenyl, butyl, and amyl chlorides,  $x$  is determined for each, and the density number for chlorine is determined from the boiling-point formula. The values found range from 3.40 to 4.44. The value given by Groshans is 4. W. S. M.

**Determination of Avogadro's Normal Volume  $V_A$  and of the Atomic Weights of Hydrogen, Helium, and Argon.** J. J. VAN LAAR (*Chem. Weekblad*, 1919, **16**, 1243—1250).—A continuation of a previous communication (A., 1919, ii, 461).

The most probable value of  $V_A$  is considered to be  $22415^3$  c.c. The atomic weights of hydrogen, helium, and argon are stated to be 1.007697 (=1.00770), 3.9998 (=4.000), and 39.95 respectively.

W. J. W.

### Molecular Attraction. III. The Characteristic Equation.

K. K. JÄRVINEN (*Ann. Acad. Sci. Fennicae*, 1919, [A], **12**, Reprint 44 pp.).—A continuation of the theoretical discussion on molecular attraction (compare A., 1913, ii, 293; A., 1915, ii, 251). The internal pressure,  $p_n$ , is calculated by the equation  $p = RT/V \cdot f - p_n$ , on the basis of the law of molecular attraction  $F = km^2/r^5$ . It is found that  $p_n = a/v^3$  for monatomic substances, and  $p_n = a/\{v\{v^{1/3} - 0.2426i\}^3\}$  for polyatomic substances, where  $a$  and  $b$  are the constants of van der Waals's equation. It is thus much smaller than that calculated from the latter equation. The critical pressure,  $p_k = RT/V \cdot f$ , is also calculated, and thence a table of values of  $f$

deduced, which may be used to find the deviations from the ideal state. Values of  $f$  are also calculated from the equations  $f = p - p_0/RT \cdot v$  and  $f = dp/dt \cdot v/R$ , the latter obtained by differentiation of the characteristic equation. These agree approximately with the theoretical values. The differences are taken to mean that the theory is yet incomplete. It is also found that  $b$  decreases with temperature, but this need not in reality be the case. The pressure, the critical data, and the values of  $v_k/b_0$ ,  $RT/pv_k$ ,  $dp/dt \cdot v/R$ , and  $dp/dt \cdot T/p$ , may be obtained with fair approximation. Only approximate accuracy is claimed.

J. R. P.

### Effects of Acids and Bases on the Surface Energy Relations of $\beta\beta$ -Dichloroethyl Sulphide (Mustard Gas).

WILLIAM D. HARRIS and D. T. EWING (*J. Amer. Chem. Soc.*, 1919, **41**, 1977—1980).—The surface tension between  $\beta\beta$ -dichloroethyl sulphide and a number of liquids has been determined with the object of finding a suitable emulsifying agent for the preparation of aqueous emulsions of this substance. The following values of the surface tension in dynes per cm. have been found between  $\beta\beta$ -dichloroethyl sulphide and the liquids named: water, 28.36; 0.1*N*-hydrochloric acid, 28.90; 0.1*N*-sodium hydroxide, 12.78; 0.1*N*-sodium carbonate, 18.82; 1% solution of turkey-red oil, 14.47; 1% solution of turkey-red oil in 0.1*N*-sodium carbonate, 8.35; 1% Twitchell's solution, 12.32; 1% Twitchell's solution in 0.1*N*-sodium carbonate, 12.89; 1% maize oil solution, 12.94; and 1% maize oil in 0.1*N*-sodium carbonate, 10.91. The surface tension of several organic liquids has also been measured:  $\alpha\alpha$ -diphenylpropane, 20°, 37.15, 25°, 36.64;  $\alpha\alpha$ -diphenylethane, 20°, 37.67, 25°, 37.20; diphenylmethane, 20°, 37.56; ditolylmethane, 20°, 35.51, 25°, 34.80; propylbenzene, 20°, 32.22, 25°, 31.30. All determinations were made by the drop-weight method.

J. F. S.

**Viscosity of Pure Liquids.** SVANTE ARRHENIUS (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 20, 1—40).—A theoretical paper, in which a large volume of work on the viscosity of liquids is discussed and correlated. It is shown that the ratio  $\eta_b \times 10^3 : \sqrt{s}$  is approximately constant for non-associated organic liquids. The symbols have the significance,  $\eta_b$  is the viscosity of a liquid at the boiling point and  $s$  is the density, and the constant varies between 230 and 320. The constant is not obtained in the case of a few liquids, which are characterised by the fact that the expression  $K_1 = T^2(d \log \eta/v^2)/dT$  does not show a minimum below the boiling point. These liquids are ethylene, propylene, and isobutylene bromides, benzene, and carbon tetrachloride. The presence of negative atoms, such as the halogens, sulphur, or oxygen, increases the value of the ratio  $\eta_b : \sqrt{s}$ . The influence of pressure on the viscosity is nearly represented by a linear equation  $\log \eta_p = \log \eta_0 + l(p - p_0)$ , where  $\eta_0$  is the viscosity at the external pressure zero (practically atmospheric pressure),  $p$  is the total pressure (external and internal) calculated according to van der Waals's



theory, and  $p_0$  the internal pressure at zero external pressure. The influence of temperature on viscosity may, for non-associated liquids, be expressed by the formula  $d \log \eta \cdot v^3/dt = K_1/T^2$ .  $K_1$  is nearly proportional to the absolute boiling point  $T_b$ , so that  $K_1 : T_b$ , if ordinary logarithms are used for calculating  $K_1$ , does not change for normal organic liquids between greater limits than 1–1.2. Benzene and the liquids named above are exceptions. For associated liquids the ratio  $K_1 : T_b$  possesses higher values, between 1.25 and 4.32. There is a pronounced parallelism between the values of the ratios  $\eta_b : \sqrt{s}$  and  $K_1 : T_b$ . In an homologous series,  $K_1 : T_b$  generally increases with the boiling point. There is a great analogy between the effect of temperature on the vapour pressure and on the product of the viscosity and the specific volume. J. F. S.

**Investigations concerning the Viscosity of Binary Liquid Mixtures.** HANS EGNÉR (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 22, 1–13).—A theoretical paper in which a large number of viscosity determinations of various authors are collected and examined in connexion with the modified logarithmic formula of Arrhenius,  $\log \eta = n_1 \log \eta_1 + n_2 \log \eta_2$ , where  $\eta_1$  and  $\eta_2$  are the viscosities of the components of the mixtures, and  $n_1$  and  $n_2$  the molecular concentrations. It is shown that this formula represents the variation of the viscosity in binary liquid mixtures more exactly than any other formula. J. F. S.

**Theoretical Significance of Viscosity Measurements of Colloidal Solutions.** SVANTE ARRHENIUS (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 21, 1–22).—A theoretical paper in which a large number of viscosity determinations of colloidal solutions are discussed. It is shown that Einstein's viscosity formula is fully established by Bancelin's results (A., 1911, ii, 586, 1067) as soon as the logarithmic formula

$$\log \eta - \log \eta_0 = \theta \phi$$

is employed. The proposed extension of Einstein's formula put forward by Smoluchowski is not confirmed by Oden's measurements on colloidal sulphur (A., 1913, ii, 485). J. F. S.

**Viscosimeter for Measuring Viscosities and Fluidities.** GEORGES BAUME and HENRI VIGNERON (*Ann. Chim. anal.*, 1919, [ii], **1**, 379–383).—The viscosimeter tube consists of a capillary provided with a bulb at its upper end and a short length of wide tube at its lower end; this tube is fixed vertically by means of a cork in a test-tube containing 20 c.c. of the oil under examination, the lower end of the tube being immersed in the oil up to a mark just below the capillary. A thermometer passes through a T-piece carried by the cork, the bulb of the thermometer dipping into the oil. The test-tube is inserted in a boiling bulb provided with a reflux apparatus. This boiling bulb may contain ether, acetone, benzene, or water, according to the temperature at which the viscosity is to be determined; when the required temperature has

been reached, the oil is forced upwards into the viscosimeter tube by a pressure ball attached to a branch of the T-piece; the pressure is then released, and the time taken for the level of the oil to fall from a mark just above the bulb (on the viscosimeter tube) to one just below it is noted.

W. P. S.

#### **Emulsification by Adsorption at an Oil-Water Interface.**

S. E. SHEPPARD (*J. Physical Chem.*, 1919, **23**, 634—639).—Emulsions of nitrobenzene in sulphuric acid and hydrochloric acid may be readily prepared by making the acid of the same density as the nitrobenzene. Similar moderately stable emulsions were prepared by saturating the acid (sulphuric) with lead sulphate or calcium sulphate, or hydrochloric acid with sodium chloride or lead chloride, in both cases the acid being of the same density as the nitrobenzene. It therefore appears that, in accordance with Bancroft's general theory of peptisation, adsorption at a liquid-liquid interface is capable of effecting emulsification. The systems thus produced, on ageing, pass into a condition approaching Pickering's emulsions, but with a great diminution of the dispersity.

J. F. S.

**Nature of Osmotic Pressure.** MITSUJI KOSAKAI (*Proc. Soc. Expt. Biol. Med.*, 1919, **16**, 118—119).—The hæmolytic effects of formaldehyde and carbamide were found to be, like that of boric acid, the result of osmotic pressure. The rates of diffusion of boric acid, formaldehyde, and carbamide are 90 sec., 30 sec., and less than 5 sec. respectively. These differences correspond with the differences in the hæmolytic action of the three substances, and confirm the view that osmotic pressure is not a direct property of a solute, but is merely water pressure developed by the process of diffusion.

CHEMICAL ABSTRACTS.

#### **Osmotic Pressure. II. The Nature of Osmotic Pressure.**

MITSUJI KOSAKAI (*J. Immunology*, 1919, **4**, 49—65).—The same degree of osmotic hæmolysis is not produced by identical concentrations of boric acid, formaldehyde, and carbamide, or by a corresponding lowering in the medium of suspension of the treated corpuscles. As the treating concentration of the three hæmolytic substances is correspondingly diminished, the ratio between that concentration and the final concentration, in the hæmolytic experiment, increases disproportionately with the different substances. The osmotic hæmolysis of corpuscles which have been treated with the three hæmolytic substances in the same osmotic concentration is not inhibited by identical concentrations of sodium chloride or of the hæmolytic substances themselves. All these facts contradict the assumption that osmotic pressure is exerted directly by the solute. Osmotic pressure is not a direct property of a solute, but is solely the pressure exerted by water which has passed, by the unexplained process of diffusion, through a semipermeable membrane to the side of the higher osmotic concentration.

CHEMICAL ABSTRACTS.

**Osmotic Pressure of an Electrolyte.** OSKAR KLEIN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 6, 1—9).—A mathematical paper in which an expression is deduced showing the connexion between osmotic pressure, concentration, temperature, and dielectric constant. The reasoning is based on thermodynamical and mechanical (kinetic) principles, and is simpler than that used by Milner (*A.*, 1913, ii, 481) in a similar problem. T. S. P.

**The Diffusion of Electrolytes into Jellies. II. The Dependence of the Diffusion on the Mobility of the Ions and the Hydration and Polymerisation of the Molecules.** OTTO VON FÜRTH and FRANZ BUBANOVIĆ (*Biochem. Zeitsch.*, 1918, 92, 139—170. Compare *A.*, 1919, ii, 13).—Diffusion in jellies differs in most cases from free diffusion in aqueous solution, and is dependent on the character of the jelly. The velocity with which acids, bases, and polymerised salts penetrate jellies is smaller than would be expected from the mobility of their ions. Weakly hydrated salts show normal diffusion (diffusion similar to that in aqueous solution) in jellies. Strongly hydrated salts, on the other hand, contrary to their behaviour in aqueous solution, diffuse relatively faster than in the previous case, so that their diffusion velocity approximates to the theoretical value obtained from the mobility of the ions. S. S. Z.

**Influence of the Concentration of Electrolytes on the Electrification and the Rate of Diffusion of Water through Collodion Membranes.** JACQUES LOEB (*J. Gen. Physiol.*, 1919, 20, 173—199).—When an aqueous solution is separated from pure water by a collodion membrane, the initial rate of diffusion of water into the solution is influenced in an entirely different way by solutions of electrolytes and of non-electrolytes. The latter influence the rate of diffusion in direct proportion to their concentration, and this effect is termed the gas-pressure effect. Solutions of electrolytes show the gas-pressure effect also, but it commences at a somewhat higher concentration than in the previous case. If the concentration of the electrolyte is below that at which the gas-pressure effect is observed, the solutions have a specific influence on the initial rate of diffusion, which is not found in the case of the solutions of non-electrolytes, and is due to the diffusion of the water in an electrified condition, the sign of the charge depending on the nature of the electrolyte in solution, according to the theory which has been advanced by the author (*A.*, 1919, ii, 497). In these lower concentrations, the curves representing the influence of the concentration of the electrolyte on the initial rate of diffusion of water into the solution show that, within a range of concentrations between  $M/256$  and  $M/16$  or more (according to the nature of the electrolyte), the reverse of what should be expected on the basis of van't Hoff's law is noticed, namely, that the attraction of a solution of an electrolyte for water diminishes with an increase in concentration. Whilst no definite assumption concerning the

origin of the electrification of water and the mechanism by which the ions influence the rate of diffusion of water particles through collodion membranes is made, it is suggested that in the lowest concentrations, attraction of the electrified water particles by the ions with the opposite charge prevails over the repulsion of the water particles by ions with the same sign of charge, whilst beyond a certain critical concentration the repelling action of the ion with the same charge as that of the water particles on the latter increases more rapidly with increasing concentration of the solute than the attractive action of the ion with the opposite charge.

It is shown that negative osmosis is due to the repulsion of the electrified particles of water by the ion with the same charge as that borne by the water.

J. C. D.

**The Effect of Strain on Solubility.** J. C. HOSTETTER (*Science*, 1919, 50, 25).—It is possible that fluctuating temperature and, perhaps, some indirect effects brought about by pressure may account for the solidification of crystals compressed in contact with their solution by loosely fitting pistons, as found by James Thomson, Le Chatelier, and Spring, without the necessity of postulating large increases in solubility due to non-uniform pressure. In preliminary experiments, individual crystals were subjected to stress at constant temperature by direct loading, and the effect on the concentration of the surrounding solution was studied by measuring the electrical conductivity. No change in concentration was found. The test was sufficiently sensitive to indicate that the effect of non-uniform pressure is much less than that produced by the same pressure acting uniformly. However, in another series of experiments, in which an unloaded crystal was placed alongside a loaded crystal, the former grew at the expense of the latter, showing that a very slight increase of solubility was produced by the stress. The method of loading the crystals has a large influence on the effects found, thus indicating the importance of the stress distribution. The experiments of Becker and Day on the linear force of growing crystals are cited as indicating the stability of a crystal in its solution, even when subjected to pressure. In their experiments, loaded crystals were found to lift the load during growth, although the pressures on the supporting edges of the crystals were finally of the order of magnitude of the crushing strength of the crystal. The evidence so far obtained indicates that the effect of strain on solubility is a second-order effect.

CHEMICAL ABSTRACTS.

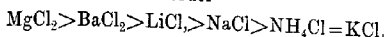
**Influence of Electrolytes on Solubility.** ERBE LINDE (*Arkiv. Kem. Min. Geol.*, 1917, 6, No. 20, 1—17).—The solubility of ethyl ether and ethyl acetoacetate has been determined in water and in solutions of certain electrolytes. In the case of ethyl ether, it is found that 7.88 grams dissolve in 100 c.c. of water at 18°. The influence of mixtures of two electrolytes on the solubility of ether in water is determined for the pairs of electrolytes, sodium

sulphate-sulphuric acid, sodium sulphate-sodium hydroxide, and sodium chloride-sodium acetate. In the first two pairs, the total electrolyte concentration was  $0.5N$ , and in the last pair  $N$ . The concentrations of the two electrolytes were varied within these limits. For the pair of electrolytes, sodium sulphate-sulphuric acid, it is shown that the solubility is 5.52 grams per 100 c.c. of  $0.5N$ -sodium sulphate, and rises regularly with decreasing sodium sulphate concentration and increasing sulphuric acid concentration to 7.72 grams per 100 c.c. of  $0.5N$ -sulphuric acid. In  $0.5N$ -mixtures of sodium sulphate and sodium hydroxide, the solubility is constant, 5.53 grams per 100 c.c. of solution, whilst in the case of sodium chloride and sodium acetate the solubility is 4.62 grams in 100 c.c. of  $N$ -sodium chloride, and falls regularly to 3.44 grams in 100 c.c. of  $N$ -sodium acetate. The electrolytes are seen, therefore, to have an additive effect. The solubility is also determined in solutions of sodium acetate and sodium chloride of varying concentration, and in both cases shown to increase steadily with increasing dilution, but in neither case is the depression of the solubility in keeping with Steiner's expression. Both sets of solubility values are fairly in keeping with the expression of Hoffmann and Langbeek (A., 1905, ii, 374). The solubility of ethyl acetoacetate has been determined in water, and solutions of sodium chloride and sodium nitrate of various concentrations at  $16-16.5^{\circ}$ . It is shown that 100 c.c. of water dissolve 12.5 grams of ethyl acetoacetate at  $16-16.5^{\circ}$ . In  $N$ -sodium chloride, 8.4 grams dissolve in 100 c.c., and this value increases with decreasing concentration of sodium chloride, but the solubility change is in keeping with neither of the above expressions. In sodium nitrate solution, 11.4 grams of ethyl acetoacetate dissolve in 100 c.c. of  $N$ -sodium nitrate, and the solubility increases in accordance with both the above-named expressions on decreasing the nitrate concentration. The addition of alcohol to solutions of sodium chloride and nitrate increases the solubility of ethyl acetoacetate in these solvents. J. F. S.

**Contrasting Effects of Chlorides and Sulphates on the Hydrogen-ion Concentration of Acid Solutions.** ARTHUR W.

THOMAS and MADEL E. BALDWIN (*J. Amer. Chem. Soc.*, 1919, 41, 1981—1990).—The hydrogen-ion concentration of a chrome tanning liquor has been determined in the presence of various concentrations of sodium chloride, ammonium chloride, sodium sulphate, ammonium sulphate, and magnesium sulphate. The effect of the addition of chlorides is to increase the hydrogen-ion concentration, whilst that of sulphates is to decrease it, although, on keeping, the concentration increases somewhat. Similar experiments were carried out with pure chromium sulphate solution, chromium chloride solution, sulphuric acid ( $0.0005N$ ), hydrochloric acid ( $0.004N$ ), sulphuric acid ( $0.1N$ ), and hydrochloric acid ( $0.1N$ ), using a number of chlorides and sulphates. In every case, the chlorides are found to increase the hydrogen-ion concentration, and

the sulphates to reduce it. The power of increasing the hydrogen-ion concentration follows the order



J. F. S.

**Degree of Ionisation of Very Dilute Electrolytes.** GILBERT N. LEWIS and GEORGE A. LINHART (*J. Amer. Chem. Soc.*, 1919, **41**, 1951—1960).—A theoretical paper in which the authors deduce a general equation for the freezing-point lowering of dilute strong electrolytes. This equation has the form  $n\lambda - \theta/c = \beta c^a$ , in which  $n$  is the number of dissociated parts,  $\lambda$  the degree of dissociation,  $\theta$  the lowering of the freezing point,  $c$  the concentration, and  $\beta$  and  $a$  characteristic constants. The calculation and observed values of  $\theta$  for fourteen salts at a series of concentrations are compared and shown to be in good agreement. The thermodynamic degree of dissociation is calculated for the same salts over a range of concentration  $10^{-1}$ — $10^{-8}N$ . The constants  $a$  and  $\beta$  of the above equation can be obtained from freezing-point determinations. The calculated degree of dissociation diverges extraordinarily from the value obtained by the usual method.

J. F. S.

**The Influence of the Dielectric Constant of the Solvent and of the Electric Energy of the Ions on Electrolytic Dissociation.** MARIO BASTO WAGNER (*Anal. Fis. Quim.*, 1919, **16**, 229—257).—A purely mathematical paper.

W. S. M.

**Mechanism of Electrolytic Dissociation.** B. CABRERA (*Anal. Fis. Quim.*, 1918, **16**, 186—225).—A mathematical paper developing the theory that the ions resulting from the solution of a crystalline substance are already present as such in the crystal, the formation of neutral molecules being thus subsequent to the act of solution or fusion.

W. S. M.

**Atomic Constitution of a Crystal Surface.** E. MADELUNG (*Physikal. Zeitsch.*, 1919, **20**, 494—496).—A mathematical paper in which the author considers the condition of the surface layer of molecules in crystals of the sodium chloride type. It is shown that in crystals of the regular type, consisting of binary compounds, the atoms of one kind on the surface are displaced in directions at right angles to the surface with respect to the atoms of the other kind. The displacement decreases in the body of the crystal according to a simple exponential equation. It is also shown that, since the atoms of electrolytes carry electric charges, an electric double layer must, in consequence of the displacement, surround the crystal surface.

J. F. S.

**A New Method of Electrical Synthesis of Colloids.** THE. SVEDBERG (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 10, 1—18).—The author has prepared gold and silver sols of high dis-

persion by a modified method. The apparatus consists of a quartz tube in which a small hole about 1 mm. diameter is bored. The metal electrodes, gold or silver, pass down this tube, and are so placed that the arc may be formed opposite the hole. The quartz tube is so arranged that a current of nitrogen passes through it both from the top and the bottom. The quartz tube is placed in an outer glass jacket containing about 30 c.c. of the dispersion medium (alcohol), and this jacket is surrounded by a further jacket containing a cooling agent (ice and salt or solid carbon dioxide and alcohol). An electromagnet is placed with its poles on either side of the small hole in the quartz tube. The current (1 amp. 220 volts) is switched on, and an arc of the usual type appears for about a second, then, owing to a melting of the lower electrode (anode), the quartz tube becomes somewhat stopped up, and so the electrode is protected from the dispersion medium; the arc becomes a sharp-pointed flame, and this is drawn through the hole in the tube by the action of the magnet. Metallic clouds appear and are absorbed by the dispersion medium. The appearance of the arc has been examined spectrographically in both conditions and the differences noted. The author holds that the condensation of metal vapour is the cause of the sol formation. Other forms of apparatus are described in the paper.

J. F. S.

**Colloid Metal Reactions. Spectrum Analysis and Blood Colouring Matter.** EDUARD RICHTER (*Kolloid. Zeitsch.*, 1919, 25, 208—211).—A number of colloid reactions between 1% gold chloride solution and 1:1000 solutions of adrenaline, alloxan, tannic acid, and *p*-phenylenedimethyldiamine are described. In each case, colloidal gold is produced, but of different degrees of dispersity. From the experiments, it is deduced that certain diamines possess a particularly powerful reducing action, and are probably to be classified with the reducing substances of the amino-group which occur in the animal organism. Certain hydroxy-substances also show a similar reducing action.

J. F. S.

**Colour of Colloids. IX.** WILDER D. BANCROFT (*J. Physical Chem.*, 1919, 23, 554—571. Compare A., 1919, ii, 500).—A continuation of the previous discussion. It is shown that with very small particles, the light which is ordinarily reflected selectively is transmitted by resonance, whilst the light which is ordinarily transmitted is scattered. Massive gold is red by multiple reflection, and thin films are green by transmitted light. Very small particles reflect green and transmit red light. Massive gold reflects yellow when compact, and brown to black when porous. Particles which do not resonate are yellow or brown by reflected light and transmit blue light. Silver is yellow by multiple reflection, and thin films are blue to green by transmitted light. Very small particles reflect blue and transmit yellow. Particles which do not resonate transmit blue light and reflect red. Colloidal indigo solutions transmit red light, and the surface colour of indigo is red. Sodium fog scatters

blue light and transmits the yellow, which the vapour absorbs. Iodine fog scatters red light. J. F. S.

**Colours of Colloids. X.** WILDER D. BANCROFT (*J. Physical Chem.*, 1919, **23**, 603—633. Compare A., 1919, ii, 500).—A continuation of the previous discussion. In the present paper the colours of glasses and glazes are considered. It is shown that in glasses and glazes, gold, silver, copper, platinum, iridium oxide, selenium, tellurium, sulphur, lead antimonate, carbon, magnetite, ferric oxide, stannic oxide, zirconium oxide, arsenious oxide, titanium oxide, and calcium phosphate occur usually as a second phase. Chromium occurs in some form as a second phase in chrome Aventurine glass and copper in Egyptian blue. Some glasses coloured by iron, chromium, manganese, and cobalt are optically empty. In enamels the substance causing the colour is probably chiefly adsorbed by the material causing the opacity. J. F. S.

**Colours of Colloids. XI.** WILDER D. BANCROFT (*J. Physical Chem.*, 1919, **23**, 640—644. Compare preceding abstract).—A continuation of the previous discussion. In the present paper the colours of gem stones are considered. J. F. S.

**Coagulation.** ARNE WESTGREN (*Arkiv. Kem. Min. Geol.*, 1918, **7**, No. 6, 1—30).—The coagulation of gold sols has been examined with the object of ascertaining the influence of the size of the colloid particles, the nature of the coagulating ions, and the temperature on the velocity of the slow coagulation. Forty c.c. of the sol were mixed with 10 c.c. of an electrolyte, and after definite intervals of time had elapsed 5 c.c. of the mixture were withdrawn and run into 25 c.c. of 0.5% gelatin solution and the particle concentration determined. Using sols with particles of radius 120  $\mu\mu$ , 77  $\mu\mu$ , and 49  $\mu\mu$  respectively, it is shown that the velocity of coagulation is independent of the size of the particles. Using the following electrolytes to coagulate the sols (hydrochloric acid, sodium, lithium, potassium and rubidium chlorides, sodium hydroxide, and sodium iodate), it is shown that the ionic conductivities of the ions are determinative of the coagulating power. Thus hydrochloric acid, the cation of which has the greatest ionic conductivity, is the most active coagulator of all the chlorides, whereas lithium chloride with its slow-moving cation is the least active. Potassium chloride and rubidium chloride, which have cations of about the same ionic conductivity, have about the same coagulating power. Since gold sols are negative colloids, it follows that when they are coagulated by cations the anions must exercise a stabilising influence, and this is shown in the coagulation by sodium derivatives, for sodium hydroxide, with its rapidly moving hydroxyl ion, is the least efficient coagulator, whilst sodium iodate with its slow-moving anion is the most efficient coagulator. Using hydrochloric acid and sodium chloride at various temperatures, it is shown that the velocity of coagulation does not depend on the temperature only, because the



Brownian movement of the particles depends on it, but also because the specific coagulation power of the electrolytes changes with the temperature.

J. F. S.

**Effect of the Wall of Vessels on the Velocity of Gaseous Reactions.** ELIHI YAMAZAKI (*J. Tokyo Chem. Soc.*, 1919, 40, 606—608).—This is a theoretical paper, attempting to give an explanation for Kooij's work (*A.*, 1893, ii, 569), in which the velocity of dissociation of phosphine was shown to be affected by the nature of the vessel, the ratio of the velocity in the new vessel to that in the old being 1 : 2.25. According to the author, the decomposition of phosphine in a vessel should be considered to be a heterogeneous chemical reaction, that is, (1) a formation of the diffused zone between gas and vessel, (2) chemical reaction. In the new vessel the wall becomes the "diffusion zone," but in the old vessel the decomposition product (phosphorus) adheres to the surface of the vessel, thus creating a larger surface which accelerates the velocity of the diffusion. Ordinarily the velocity of the diffusion of the gas over the wall is so fast that only the velocity of the chemical reaction is measured as the total reaction velocity. The author believes that the vessel acts as a catalyst in the same manner as platinum black or sponge, by removing the product of the reaction, thus maintaining general equilibrium. More detailed investigation and explanation are promised. CHEMICAL ABSTRACTS.

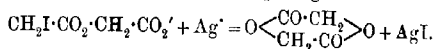
**An Unsolved Problem in the Application of the Quantum Theory to Chemical Reactions.** W. C. M. LEWIS (*Phil. Mag.*, 1920, [vi], 39, 26—31).—On applying the quantum theory to a unimolecular reaction, it is shown that very different results are obtained according as it is assumed that the absorption of radiation is continuous or discontinuous. A very large discrepancy exists in both cases between the calculated and observed velocity constants, which is much greater on the discontinuous view than on the continuous. This discrepancy is always in the sense that the observed velocity constant is many times greater than the calculated; on the hypothesis of continuous absorption, the observed constant is of the order of  $10^7$  times greater than the calculated, and also appears to be independent of temperature, for different reactions. The explanation of this discrepancy is expected to throw light on the theory of physicochemical processes. J. R. P.

**The Propagation of Flame in Mixtures of Methane and Air. I. Horizontal Propagation.** WALTER MASON and RICHARD VERNON WHEELER (*T.*, 1920, 117, 36—47).

**The Propagation of Flame in Complex Gaseous Mixtures. IV. The Uniform Movement of Flame in Mixtures of Methane, Oxygen, and Nitrogen. "Maximum-speed Mixtures" of Methane and Hydrogen in Air.** WILLIAM PAYMAN (*T.*, 1920, 117, 48—58).

**Hydrolysis of Iodoacetic Acid.** BROR HOLMBERG (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 11, 1—12).—The velocity of replacement of iodine by hydroxyl in the sodium and barium salts of iodoacetic acid by the action of sodium and barium hydroxides has been studied; the influence of neutral salts (sodium chloride and iodide and barium chloride) was also investigated. The reaction is bimolecular, its velocity being intermediate between those observed for the corresponding bromo- and chloro-acids (compare Johansson, A., 1912, ii, 544). Contrary to expectation, therefore, iodoacetic acid is more stable than bromoacetic acid (compare Drushel and Simpson, A., 1918, i, 57). The effect of the concentration of the metal ions on the velocity constant,  $C$ , is given by the equations  $C = 0.106[\text{Na}']^{0.1}$  and  $C = 0.220[\text{ba}]^{0.2}$ , where  $\text{ba} = \frac{1}{2}\text{Ba}$ .

The reaction between iodoacetic acid or its salts and silver nitrate was also studied. The formation of silver iodide takes place much more quickly than the production of acid, and the author concludes that the most important reactions are represented by the equations:  $2\text{CH}_2\text{I}\cdot\text{CO}_2' + \text{Ag}' = \text{CH}_2\text{I}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CO}_2' + \text{AgI}$  and



If the solutions are not too dilute, the formation of iodoacetyl glycollic acid takes place much more quickly than the formation of glycollic acid. Glycollic acid is then formed indirectly, or it may also be formed directly, according to the equation  $\text{CH}_2\text{I}\cdot\text{CO}_2' + \text{Ag}' + \text{H}_2\text{O} = \text{OH}\cdot\text{CH}_2\cdot\text{CO}_2' + \text{H}' + \text{AgI}$ .

T. S. P.

**Effect of Chlorine on Periodic Precipitation.** [Miss] A. W. FOSTER (*J. Physical Chem.*, 1919, 23, 645—655).—When silver nitrate is allowed to diffuse into gelatin films containing potassium chromate, a series of concentric rings is formed, the spacing of which decreases with the distance from the centre. The appearance and spacing of these rings does not depend on the time which has elapsed between the formation of the gelatin film and the addition of the silver nitrate. If, however, a trace of chloride is present in the gelatin the appearance is altered. Making up the gelatin chromate solution with tap water is sufficient to produce the change. If such a film is allowed to harden for three hours and then treated with silver nitrate, the rings are spiral in form and in groups of three. If a little calcium hypochlorite is added to the gelatin and the film allowed to harden for an hour, narrow rings close together are formed by two precipitations.

J. F. S.

**Some Problems in Contact Catalysis.** WILDER D. BANCROFT (*Trans. Amer. Electrochem. Soc.*, 1919, 36, reprint).—A number of specific cases of catalytic reactions are cited where a satisfactory explanation of the mechanism of catalysis is not available, and further study of these is suggested. Thus, the reaction  $\text{COCl}_2 + \text{H}_2\text{O} = \text{CO}_2 + 2\text{HCl}$  is, so far as is known, irreversible. In the presence of excess of water the reaction goes to completion, but in the presence of concentrated hydrochloric acid the rate of hydrolysis is

negligible. A theory is suggested, but study is necessary to prove it. Also, trichloromethyl chloroformate (superpalite) reacts as follows in the presence of alumina:  $\text{CCl}_3\cdot\text{O}\cdot\text{COCl}=\text{CO}_2+\text{CCl}_4$ , and in the presence of ferric oxide,  $\text{CCl}_3\cdot\text{O}\cdot\text{COCl}=2\text{COCl}_2$ . The reverse reaction has never been made to take place to any extent. Yet, when some superpalite and ferric oxide were placed in a tube the reaction soon came to an apparent end. When the temperature was raised a little the reaction went further and did not reverse on cooling. It is suggested that this phenomenon was due to poisoning of the ferric oxide. Finally, some experiments by Lind are cited which may, if desired, be regarded as the displacement of an equilibrium by a catalytic agent. If radium emanation is placed in water in the liquid phase, hydrogen and oxygen are formed and escape into the vapour phase; if the emanation is moved up into the vapour phase oxygen and hydrogen are caused to combine. Additional examples are cited and some interesting lines of experiments suggested.

#### CHEMICAL ABSTRACTS.

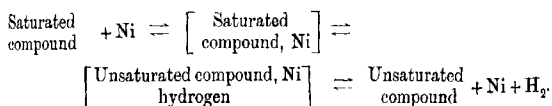
**Catalytic Decomposition of Hydrogen Peroxide.** GÖSTA PHRAGMÉN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 22, 1—13).—The rate of decomposition of hydrogen peroxide in alkali phosphate or sodium hydroxide solutions has been determined at 17—18°. In the phosphate mixtures, it is shown that the reaction velocity reaches a maximum at  $P_{1/2}=11.8$ . In alkaline hydroxide solutions, the velocity is not easily reproducible, and sometimes gives a large value and sometimes a small value. Since the velocity decreases with both increasing and decreasing hydrogen-ion concentration, it is assumed that hydrogen peroxide forms a salt with sodium hydroxide which is very stable, and that only the undissociated hydrogen peroxide molecules undergo decomposition. The decomposition of hydrogen peroxide by yeast extract in the presence of a phosphate buffer mixture has been determined at 17—18°. It is shown that fresh yeast decomposes dilute hydrogen peroxide without sending a soluble enzyme into the surrounding liquid. The reaction is of the first order between certain limits, and the reaction coefficient increases proportionally to the quantity of yeast. The catalytic action per cell or per gram can be increased by treating the yeast with sugar solution before use. The reaction constant is no criterion of the quantity of catalase in the cells.

J. F. S.

**Catalytic Actions at Solid Surfaces. II. Transference of Hydrogen from Saturated to Unsaturated Organic Compounds in the Liquid State in Presence of Metallic Nickel.** E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1919, [A], 96, 322—329. Compare A., 1919, ii, 403).—The evidence that metallic catalysts, during the hydrogenation process, interact primarily with the unsaturated organic compound, together with the resemblance of the whole process to enzyme action (*loc. cit.*), led to the consideration whether the catalytic action, like that

of certain enzymes, might not be reversible. Evidence in support of this view has now been obtained. At 180°, an equimolecular mixture of *cyclohexanol* and methyl cinnamate may, in the presence of nickel, be transformed into one in which about 10% of the cinnamic ester has become hydrogenated to methyl  $\beta$ -phenylpropionate, the *cyclohexanol* being transformed into *cyclohexanone*. The experiments indicate that it is necessary that both components of the system should be present in the liquid state. A similar action took place to a certain extent at 230°, when the *cyclohexanol* was replaced either by dimethyl*cyclohexane* or by dihydropinene. Similarly, a mixture of ethyl stearate and methyl cinnamate when heated at 230° with catalytic nickel gave a product containing small quantities of methyl  $\beta$ -phenylpropionate and ethyl oleate. An important point to note is that simultaneous dehydrogenation and hydrogenation have now been effected at temperatures not far removed from the general optimum hydrogenation range (170–180°), and that hydrogen has been transferred from one compound to another, instead of from one molecule to another of the same species, as was observed by Zelinski and Glinka (compare A., 1911, i, 870).

There is no absolute proof that the mechanism of the change is not dependent on the production of hydrides of nickel, but the authors prefer to regard it as a further case of the catalytic equilibria, previously discussed, which may be indicated as follows:



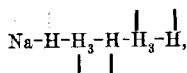
The ultimate equilibrium will depend on the resultant of the varying affinity for nickel of the saturated and unsaturated compounds involved.

This view of catalytic hydrogenation and dehydrogenation affords some explanation of the products obtained (compare Moore, *J. Soc. Chem. Ind.*, 1919, **38**, 320r) during the hydrogenation of unsaturated glycerides, where partial isomerisation occurs. It is suggested that, in the hydrogenation of ethyl oleate, a portion of the freshly produced ethyl stearate in contact with the nickel undergoes dehydrogenation, the hydrogen liberated being transferred to more ethyl oleate, the 'dehydrogenated ethyl stearate' formed being the ethyl  $\Delta^7$ -oleate isolated by Moore (*loc. cit.*). W. G.

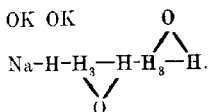
### Constitution and Structure of the Chemical Element.

HAWKSWORTH COLLINS (*Chem. News*, 1919, **119**, 295–296).—Single electropositive charges emanate from masses of 1 (hydrogen), 7 (lithium), 23 (sodium), and 39 (potassium), also two electropositive charges emanate from 4 (helium), of which one has been shown to emanate from a mass 3 ( $\text{H}_3$ ), hence single electropositive charges emanate from masses 1, 3, 7, 23, 39. Taking the first twenty-six elements, it is shown that twenty of these may have their

atomic weights split up into the above-named numbers in such a way that the number of parts is the same as the maximum valency. All the parts are odd numbers, and the non-metallic elements are characterised from the metallic by the presence of one or more portions (1+3) (helium). Electropositive forces are distinguished from electronegative forces by the following rule: an electropositive force emanates from each of the masses 1, 3, 7, 23, 39, except when an element has one or more portions (1+3), in which cases electropositive forces emanate from these portions, whilst electronegative forces emanate from each of the remaining portions of the element. Hydrogen forms the connecting link in the structure of these elements. From tables given in the paper, it is shown that the longer the chain of  $-H-H_3$ , the more volatile the element and the stronger the electronegative forces from the metallic portions. On this basis, the structure of the sulphur atom is given as



in which Na represents 23, H represents 1, and  $H_3$  3. The thick lines represent electropositive charges, the curly lines electronegative charges, and the thin lines forces which are not chemically evident, but which have to be overcome before the element can be disintegrated. The atomic number of sodium is 11, that of H and  $H_3$  unity, which makes the atomic number of sulphur 16, which is in keeping with fact. The formula therefore shows the connexion between atomic weight, atomic number, and maximum valency, and distinguishes between electropositive and electronegative charges. The molecule  $K_2SO_4$  may therefore be represented:



J. F. S.

**A Model of Radioactive Atoms.** TORAHIKO TERADA (*Proc. Phys. Math. Soc. Japan*, 1919, [3], 1, 185—195).—According to the recent view of atomic structure, an atom consists of a positive nucleus about which a number of electrons are revolving. The conception of the positive nucleus is slightly extended by considering the case of two heavy nuclei with opposite charges revolving about the common centre of mass. Assuming a primary with the larger mass having a positive resultant charge, and the secondary of smaller mass charged negatively as a whole, and leaving out of consideration the ring electrons, it is evident that the two members of the nuclear system will exert on each other a mutual action analogous to the tidal action in the case of the gravitating planetary system. Both members are considered to consist of a number of positive and negative elementary charges, bound together by some unknown forces; also most of the positive charges are assumed to

consist of two elementary charges, as in the case of  $\alpha$ -particles. When the tidal action exceeds a certain limit, the secondary may become unstable, and when the elementary charges in the two substances happen to take a definite configuration, one of the charges may escape and be projected from the nuclear system with the momentum possessed during the orbital motion. If the negative secondary loses a positive charge by the expulsion of an  $\alpha$ -particle, the attraction of the primary will increase, and the orbital velocity be accelerated. In actual radioactive transformations, the velocities of the expulsion of the  $\alpha$ -particles generally increase with successive transformations, although with some exceptions. The tidal action will increase with the decreasing distance between the two nuclei, and consequently the chance of disruption will increase, because the chance of the  $\alpha$ -particle stepping out of the critical threshold will increase. The result will be the shortening of the life of the atom in question. This seems to suggest a possible way of explaining Geiger and Nuttall's law concerning the relation between the average lives of radio-elements belonging to a disintegration series and the velocities of the  $\alpha$ -particles emitted from these elements. If the two members of the nuclear system gradually approach each other by successive emission, a stage may be attained at which the two substances are amalgamated into one, provided the resulting configuration is a stable one. When this final stage is reached, the disintegration will be stopped and the end-product of the radioactive transformation will be reached. One of the simplest systems conceivable is proposed as a provisional working model, and the consequences tested in the light of the available experimental data.

CHEMICAL ABSTRACTS.

**Metals and Non-metals.** A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 119–125).—The author explains the positive charge of the chlorine electrode by assuming that the chlorine atom has the power of splitting off and absorbing electrons, and, further, that these two processes can take place side by side. This is represented by the equations  $XCl_{2e} \rightleftharpoons 2XCl_e' + 2X\ominus_e$  and  $YCl_{2e} + 2Y\ominus_e \rightleftharpoons 2YCl_e'$ , in which  $X'$  and  $Y$  indicate the fractions of the chlorine molecules which have undergone positive and negative ionisation respectively. As the electrons which are absorbed in the second action proceed from the first, it is clear that  $Y \leq X$ , but, chlorine being a non-metal, both fractions must be extremely small. If, then, it is further assumed that the negative ions almost exclusively pass into solution, the electrode will then possess a positive charge. Extending the above hypothesis, the author shows that there is only a difference of degree between metals and non-metals, and not one of kind. If it be assumed that all elements can both split off and absorb electrons, then the factor  $X$  is comparatively large for metals and small for non-metals, and for non-metals  $Y$  is exceedingly small. This view is in keeping with the large electric conductivity of metals and the small conductivity of non-metals. In the case of the metals, the

positive ions have the greater solubility, and the negative ions in the case of the non-metals. This is in keeping with the different electromotive behaviour of metals and non-metals. The difference in solubility between the two ions is so great as to justify the assumption that only one kind is present in solution. Amphoteric elements probably send appreciable quantities of both positive and negative ions into solution.

J. F. S.

**Atomic Structure and the Periodic Law.** TYCHO ESOX AURÉN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 18, 1—7).—A theoretical paper. The author's experiments on the absorption of Röntgen rays (details not yet published) indicate the possibility of differentiating between the inner and outer electrons in the atom, the outer electrons being identical with the so-called valency electrons and playing a totally different rôle from the inner electrons. In accordance with this view, Kossel's table (A., 1916, ii, 243) for the first twenty-three elements of the periodic system is modified. The number of electrons in the outer ring increases from one in the case of hydrogen to seven in the case of nitrogen; it does not become eight in the case of oxygen, but four electrons go from the outer ring to the inner system; the number of outer electrons then increases to seven again for sodium, whilst for magnesium four more electrons go from the outer to the inner system, and so on. The consequences of these conceptions are discussed, special reference being made to the valencies of the elements in the various groups. For example, it is argued that sulphur should be bivalent; the existence of  $\text{SO}_3$  and  $\text{SF}_6$  is no definite proof of the sexavalency of sulphur, since the former can be represented by a ring structure and the latter as  $\begin{matrix} \text{F} & & \text{F} \\ & \diagdown & / \\ & \text{S} & \\ & / & \diagdown \\ \text{F} & & \text{F} \end{matrix}$  T. S. P.

**Atomic Numbers.** HAWKSWORTH COLLINS (*Chem. News*, 1919, 119, 285—287).—The author considers the atomic weights (nearest whole number), atomic numbers, and valencies of the first twenty-eight elements, taken in order of their atomic weights. It is shown that, with four exceptions (glucinum, nitrogen, scandium, and cobalt), when the atomic weight is represented by an even number, the maximum valency and the atomic number are both represented by even numbers, and when the atomic weight is represented by an odd number, the valency and the atomic number are also represented by odd numbers. Further, the elements, with the exceptions named, follow one another alternately odd and even. The probability that this condition of things has happened accidentally is  $1:4^{28}$ . The reason for the odd and even rule is shown to be as follows. If the atomic weight of an element be split up into 3's and 1's alternately, always commencing with a 3, the number of portions obtained gives the atomic number, and should the atomic number be an even number, the atomic weight must of necessity be an even number, but if the atomic number is odd, the atomic weight must also be odd. The atomic number is exactly

obtained as follows. If the atomic weight is an even number, the atomic number is one-half of the atomic weight, but if the atomic weight is an odd number, the atomic number is one-half of the atomic weight from which 1 has been subtracted. J. F. S.

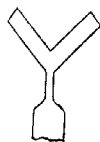
**The Mathematical Possibility of Increasing the Yield or of Reducing the Proportion of the Reacting Substances in certain Chemical Reactions.** ANGEL PÉREZ HERNÁNDEZ (*Anal. Fis. Quim.*, 1918, **16**, 302—317).—An elementary mathematical method is illustrated for the construction of chemical equations in which two or more reactions are simultaneously involved.

W. S. M.

**Some Biographical Notes on Hermannus Follinus.** W. P. JORISSEN (*Chem. Weekblad*, 1919, **16**, 947—951).—The biographer gives a very brief sketch of Hermannus Follinus, who was born in Friesland, circa 1590, and joined the medical faculty in Cologne, where he died of the plague in 1622. He was the author of "Den Nederlandtsche Sleutel van't Secreet der Philosophie" (Key to the Secrets of Philosophy), "Physiognomie," and "Simonides, ofte die Memori-const" (Science of Memory).

W. J. W.

**An Apparatus for Preparing in a Very Short Time Homogeneous Liquid Mixtures.** PIERRE JOLIBOIS (*Compt. rend.*, 1919, **169**, 1095—1098).—A simple apparatus is described consist-



ing essentially of two containers, one for each of the liquids to be mixed, arranged so as to deliver into the two limbs of a Y-tube of the pattern shown the liquids in the requisite proportion. The diameter of the Y-tube is 6.2 mm., and the lower limb has a restriction as shown 1.5 mm. in diameter and 2 cm. long. With such an apparatus a homogeneous mixture may be obtained

from two miscible liquids in 1/100th of a second.

W. G.

**Eykman's Suction Pump.** L. TH. REICHER (*Chem. Weekblad.*, 1919, **16**, 951—956).—This apparatus embodies the principle of Zeissler's suction pump, but the operation of filling the vessel in communication with the apparatus which has to be exhausted, by lifting a second vessel periodically, is avoided. Special features of Eykman's pump are a "vacuum reservoir," containing air-free, concentrated sulphuric acid, and a drying device also filled with that liquid. A sketch of the complete apparatus is given and its mode of operation described.

W. J. W.



## Inorganic Chemistry.

**Model of a Triatomic Hydrogen Molecule.** N. BOHR (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 28, 1—16).—A theoretical paper in which it is shown that triatomic hydrogen consists of three nuclei and three electrons. The electrons rotate at equal angular intervals in a common circular orbit, whilst the three nuclei are placed on the axis of this orbit. It is shown that  $H_3$  cannot be formed from  $H_2$  molecules without the supply of energy from external sources. On the other hand, it is shown that in hydrogen gas which is ionised by external agencies, molecules of  $H_3$  may be formed by successive processes, each of which is accompanied by the production of heat. J. F. S.

**The Solubility of Sulphur Dioxide in Sulphuric Acid.** FRANK DOUGLAS MILES and JOSEPH FENTON (*T.*, 1920, 117, 59—61).

**Some Points of View concerning the Nitrogen Question and Related Problems.** L. HAMBURGER (*Chem. Weekblad*, 1919, 16, 560—595).—An amplified version of a lecture delivered before the Algemeen Bestuur der Nederlandsche Chemische Vereeniging on July 13th, 1918. W. S. M.

**Electrochemical Reactions of Nitrogen and the accompanying Spectroscopic Phenomena.** L. HAMBURGER (*Chem. Weekblad*, 1918, 15, 931—942).—A mixture of nitrogen and hydrogen in stoichiometrical proportions under a pressure of 12 mm. of mercury was passed through a quartz capillary tube and subjected to a direct-current discharge of 12 amperes per square cm. A yield of 109 mg. of ammonia per kilowatt-hour was obtained. Reduction of the current density and simultaneous increase of the time of exposure to the discharge gave much smaller yields. The conditions for a high yield of ammonia thus correspond with those necessary for the formation of activated atomic nitrogen and hydrogen. The discharge through mixtures of nitrogen with hydrogen, oxygen, and carbon monoxide was examined spectroscopically. In every case evidence of the disruption of the molecules and formation of new compounds, such as cyanogen, was obtained. W. S. M.

**The Dissociation Constant of Nitrogen Peroxide.** EUGÈNE WOURTZEL (*Compt. rend.*, 1919, 169, 1397—1400).—As a result of measurements at temperatures between 0° and 86.5° it is shown that the variation of the dissociation constant with the temperature is given by  $\log K/T = 8.9908 - 2810.5/T$ , and calculated from this the heat of polymerisation is 12,850 cal., exact to 0.5%. W. G.

**Luminescence and Ionisation in the Oxidation of Phosphorous Oxide.** HERMAN RINDER (*Arkiv Kem. Min. Geol.*, 1917-18, 7, No. 7, 1—21).—A mixture of oxygen and carbon

dioxide, dried by means of sulphuric acid, calcium chloride, and phosphoric oxide, and warmed to a suitable temperature, is passed through two absorption bulbs containing phosphorous oxide, with the vapour of which it becomes saturated. No luminescence takes place with the dried gas, but when the mixture is led over the surface of water contained in a test-tube, luminescence appears. The absorption bulbs and test-tube containing water were immersed in a thermostat at constant temperature, and the total intensity of the luminescence was measured photographically by means of a Martens' photometer.

There is no luminescence in pure carbon dioxide, but the addition of oxygen causes the phenomenon to appear, and its intensity is greatest in mixtures containing 5% of oxygen. With increase in the percentage of oxygen the intensity decreases and attains an approximately constant value between 50% and 100% oxygen (compare Scharff, A., 1908, ii, 373). When a tube, 3.75 metres long, is inserted between the absorption bulbs and the test-tube, the intensity of the luminescence is about the same for mixtures containing a low percentage (about 5%) of oxygen, but it rapidly diminishes with increasing oxygen content to a lower value than before the tube was inserted. At the same time the tube becomes covered with a deposit of phosphoric oxide. These results indicate that the phosphorous oxide is oxidised without luminescence by the dry oxygen, and that the diminished luminescence with mixtures containing high percentages of oxygen is due to the fact that the gas coming into contact with the water-vapour contains much less phosphorous oxide.

According to Scharff (*loc. cit.*), the merest trace of water-vapour is sufficient to cause luminescence, but the author finds that when the vapour pressure of the water-vapour is diminished, as, for example, by using concentrated sulphuric acid instead of water, the luminescence becomes very feeble.

As with all gas reactions, the width of the test-tube containing the water affects the intensity of the luminescence. The wider the test-tube the less the luminescence.

The author suggests that in dry oxygen phosphorous oxide is directly oxidised to phosphoric oxide, but that in moist oxygen an intermediate compound, X, is formed, according to the equation  $P_4O_6 + H_2O + O_2 \rightarrow X \rightarrow H_3PO_4$ .

Ionisation does not occur in a gas free from oxygen, but containing phosphorous oxide. In the presence of oxygen ionisation takes place, and the author has measured the saturation current (compare Harms, A., 1904, ii, 331; Bloch, A., 1905, ii, 72). The ionisation is not a photoelectric effect, as shown by measurement of the saturation current with different electrodes, but is caused by the oxidation of an unknown intermediate product formed from phosphorous oxide and water vapour. The mobility of the ions is small compared with that of ordinary gaseous ions, but of the same order as that obtained for the ions formed in the oxidation of phosphorus (compare Harms and Bloch, *loc. cit.*), and it is very probable that the ions are produced by the same reaction in both cases. T. S. P.

**Some Chemical Characters of Ancient Charcoals.** T. C. CANTRILL (*Archaeol. Cambrensis*, 1919, 365—392).—Although the pieces of charcoal or charred wood found during archaeological excavations are more readily attacked or dissolved by such reagents as nitric acid and potassium chlorate, and hypochlorite solution, thus differing from modern, well-burnt charcoal, the author considers that the solubility, etc., of some of the ancient charcoals is simply due to their incomplete carbonisation, and that there is doubt that they were produced by the agency of fire. The situations in which certain of the charcoals are found negatives the opinion that the blackening of wood was due to the action of peaty soil. W. P. S.

**Artificial Production of Diamond.** SIR CHARLES ALGERNON PARSONS (*Phil. Trans.*, 1919, A, 220, 67—107).—Bakerian lecture. It is shown from experiments that all the hydrocarbons, chlorides of carbon, and oxides of carbon deposit amorphous carbon or graphite on a carbon rod electrically heated at any pressure up to 4400 atms. and in a few cases up to 6000 atms. At 15,000 atms. carbon and graphite electrically heated are either transformed into soft graphite or are first vaporised and condensed as such. The experiment of compressing a mixture of acetylene and oxygen and the production of a temperature in excess of that required to vaporise carbon, accompanied by a momentary pressure of 15,000 atms., shows that the failure to convert graphite into diamond is not due to lack of temperature. The experiment of firing a high-velocity steel bullet with cupped nose through vaporising carbon into a hole in a block of steel raises the pressure momentarily to 300,000 atms. and the temperature probably 1000°, but the fact that only a few minute crystals resembling diamond were produced (probably from the iron) leaves a doubt as to whether the duration of the pressure was sufficient to start a recognisable transformation of graphite to diamond. A repetition of many of the experiments, in which diamond has been claimed to be formed, has given negative results except where iron has played a part. A list of the experiments tried together with conditions and results is given in an appendix to the paper. In repeating Moissan's experiments it is shown that when a crucible of molten iron is subjected to pressure more than three times as great as can be produced by these contractile forces, the yield of diamond is not increased; on the other hand, if the occluded gases are imprisoned, then the yield of diamond is about the same as when the crucible is plunged into water, whilst if the conditions are such as to allow a free passage of the gases through the skin of the ingot the yield is at once reduced, even though the bulk pressure on the ingot is the same. Experiments in vacuum, from 75 mm. to X-ray vacuum, show generally that as the pressure is decreased the yield of diamond is diminished, and below 2 mm. no diamond could be detected. The greatest percentage of diamond occurred when the atmosphere round the crucible consisted of 95% carbon monoxide, 1% hydrogen, 2% hydrocarbons, 2% nitrogen. The weight of diamond is about 1/20,000 of the weight of the iron. It appears that the formation of diamond in rapidly cooling iron takes

place when it is solid or in a plastic condition or even at a lower temperature. The rapid pitting of a diamond in highly carburised iron just above its melting point is so pronounced that the largest diamond hitherto produced artificially would be destroyed in a few seconds if the iron matrix were molten. The experiments indicate that the bulk pressure on the metal does not play a part in the formation of diamonds, but that the previous heat treatment, the impurities in the iron, and the condition of the gases within the metal are the important factors. The iron in the most successful experiment has a concentration of diamond 270 times as great as the blue ground in the South African mines.  
J. F. S.

**Production of Carbon Monoxide in the Flames of Gases.** ANDRÉ KLING and DANIEL FLORENTIN (*Compt. rend.*, 1919, 169, 1404—1406).—A number of gases, the carbon monoxide content of which varied from 0% to 60%, were burnt at differing types of burners in a large chamber, and the carbon monoxide in the air was estimated at the end of one hour. The results indicate that the production of carbon monoxide is due principally to the sudden cooling of the flame. For a given type of burner the amount of carbon monoxide present in the gas to be burnt is without influence on the amount present in the products of combustion. The Auer burner produced comparatively large amounts of carbon monoxide, this production being due apparently to the presence of the incandescent mantle. The hourly production of carbon monoxide with certain common types of burners is sufficiently high to warrant further efforts to improve them.  
W. G.

**Atomic Structure of Metals in Solid Solution.** A. L. FEILD (*Chem. and Met. Eng.*, 1919, 21, 566—570).—The reason for the difference in physical properties of solid solution alloys and their components has been investigated. It is concluded that the alloys retain in the solid state the same atomic structure as in the liquid state, the metals being in the amorphous form. Such a solid solution is analogous to a supercooled liquid with the same electrical resistance and temperature-coefficient of resistance as in the molten state. Experiments with alloys of nickel and chromium, and of gold and silver, confirm this theory. It does not apply to eutectic alloys. The hardness of alloys is also ascribed to an amorphous state.  
W. J. W.

**Transition of Dry Ammonium Chloride.** ALEXANDER SMITH, HERBERT EASTLACK, and GEORGE SCATCHARD (*J. Amer. Chem. Soc.*, 1919, 41, 1961—1969).—Time-temperature curves, both heating and cooling, have been made for absolutely dry ammonium chloride with the object of ascertaining whether the dry material changes into a second crystalline form at 184.5°, as does the undried material. It is shown that ammonium chloride which has been dried for forty-five days at 155—165°, or for three years with phosphoric oxide in a high vacuum, undergoes exactly the same transition at 184.5° as the undried salt. In the thermal measure-

ment of transition points in a high vacuum confusion may result from the greater thermal effects of distillation. Wegscheider's explanations of the anomalous vapour density of dried ammonium chloride by a failure to undergo transition in the absence of water are untenable in the light of these results (A., 1918, ii, 298).

J. F. S.

**Lithium Silicate.** K. ALB. VESTERBERG (*Medd. K. Vetenskapskad. Nobel-Inst.*, 1919, 5, No. 30, 1—9).—Amorphous silicic acid, which has been dried at 100°, dissolves slowly in a fairly concentrated (approx. 2*N*) solution of lithium hydroxide at the ordinary temperature, giving finally a solution containing 3.4 mols. of  $\text{SiO}_2$  to 1 mol. of  $\text{Li}_2\text{O}$ . Thus lithium behaves similarly to potassium and sodium in giving soluble silicates containing a large excess of acid over the base (compare A., 1915, ii, 344; also Jordis and Kanter, A., 1903, ii, 475, 542, 595; Jordis, 1908, ii, 291; Ordway, 1908, ii, 37). In warm lithium hydroxide solution, however, silicic acid is almost insoluble, the acid being transformed into a practically insoluble lithium silicate.

*Lithium metasilicate* occurs in two modifications, the one easily soluble and the other almost insoluble. The latter, which has the formula  $\text{Li}_2\text{SiO}_3 \cdot \text{H}_2\text{O}$ , is obtained as a white, granular precipitate when a fairly concentrated solution of sodium metasilicate is mixed with the equivalent quantity of lithium chloride, lithium hydroxide added in approximately normal concentration, and the solution heated for a short time at 80—90°. It can also be obtained by dissolving silicic acid, which has been dried at a temperature not higher than 100°, in twice the theoretical amount of 2*N*-lithium hydroxide solution at the ordinary temperature, and then heating the solution for a short time at 80°.

T. S. P.

**A New Physicochemical Method of Analysis of Precipitates. Application to the Study of the Calcium Phosphates.**

PIERRE JOLIBOIS (*Compt. rend.*, 1919, 169, 1161—1163).—The two solutions, from which the precipitate is obtained, are very rapidly mixed by means of the apparatus previously described (this vol., ii, 107), and the precipitate is collected and analysed and the supernatant liquid is also analysed when equilibrium has been reached. Applying this method to the study of mixtures of solutions of calcium hydroxide and phosphoric acid in varying proportions, the author has prepared and characterised a new calcium phosphate having the composition  $2\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$ . This phosphate occurs in a crystalline form, and in the presence of excess of phosphoric acid is slowly converted into the dicalcium phosphate.

W. G.

**Research on Magnesia Alba by Joseph Black, Petrus Driessen and Others.** W. P. JORISSEN (*Chem. Weekblad*, 1919, 16, 1579—1589).—The author gives a retrospect of the researches of Joseph Black on magnesia alba, which led to his discovery of carbon dioxide ("fixed air"). The methods of preparation of

magnesia alba, described in the literature on the subject, are variations of the original experiments of Black, Driessen, and other investigators of the eighteenth century. W. J. W.

**Zincates of Sodium. Equilibria in the System  $\text{Na}_2\text{O}-\text{ZnO}-\text{H}_2\text{O}$ .** F. GOUDRIAAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 179—189).—The solubility isotherm in the system  $\text{Na}_2\text{O}-\text{ZnO}-\text{H}_2\text{O}$  has been completely determined at  $30^\circ$  by dissolving zinc oxide in solutions of sodium hydroxide of various concentrations and determining the solubility. The following substances appear as stable, solid phases: zinc oxide, sodium zincate,  $\text{Na}_2\text{O}\cdot\text{ZnO}\cdot 4\text{H}_2\text{O}$ , and the monohydrate of sodium hydroxide. Sodium zincate forms very strongly incongruent solutions; in solutions containing 1 part of sodium hydroxide to 2 parts of water, it is decomposed, with separation of zinc oxide. Amorphous, gelatinous zinc hydroxide is to be regarded as a phase of a varying water content; it is impossible to remove all adsorbed ions from it, and it is metastable as regards zinc hydroxide. In special circumstances zinc hydroxide may be obtained as a crystalline phase of the constant composition,  $\text{Zn}(\text{OH})_2$ . This crystallised hydroxide is metastable at  $30^\circ$  with respect of zinc oxide. J. F. S.

**Reguline Lead Peroxide.** WILH. PALMAER (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 31, 1—15).—Compact lead dioxide has been prepared by the electrolysis of lead nitrate solution. The product is greyish-black in colour and has a pronounced crystalline appearance, and contains no impurities; it has a hardness 5—6 and D 9.360. In all respects it is similar to the mineral plattnerite. The specific resistance at  $18^\circ$  is  $0.000845$  ohm and the specific conductivity  $1180$  ohm $^{-1}$ . The temperature-coefficient of the conductivity is  $1/8\%$  per degree. J. F. S.

**Aluminium Spontaneously Oxidisable in the Air.** E. KOHN-ABREST (*Compt. rend.*, 1919, **169**, 1393—1395).—Attention is drawn to the fact that when aluminium is distilled in a vacuum at  $1100^\circ$ , the globules of aluminium remaining undistilled at the end of sixteen to twenty hours, when exposed to the air at the ordinary temperature, undergo spontaneous oxidation, giving a yellowish-grey powder, which is a mixture of the oxide and the finely divided metal. This aluminium only contained 0.4% of iron and 0.5% of silicon. W. G.

**Chemical Method for the Determination of the Strength of Sparingly Soluble Inorganic Bases.** K. A. VESTERBERG (*Arkiv. Kem. Min. Geol.*, 1917, **6**, No. 11, 1—20).—The determination of the hydrolysis of salts of sparingly soluble inorganic bases by electrometric methods and methods depending on the inversion of sucrose or the hydrolysis of esters has given very varying results, according to the methods used (compare Denham, T., 1908, **93**, 41; Lundén, A., 1908, ii, 164). Farmer's method (T.,

1901, 79, 863) for the determination of hydrolysis does not give correct values, owing to the disturbance of the hydrolytic equilibrium by the partial extraction of the one product of hydrolysis. In the case of cobalt acetate, for example, too little acetic acid is extracted. The author makes use of Farmer's method, but modifies and corrects it as follows. The solution is extracted with twice its volume of ether; the same ethereal solution is again used to extract half its volume of a fresh solution of cobalt acetate. This process is repeated until the concentration of the ether phase becomes constant with respect to acetic acid, showing that it is in equilibrium with hydrolysed cobalt acetate solution, in which base and acid are present in equivalent proportions. The percentage hydrolysis can then be readily calculated. Usually, the concentration of the ether phase becomes constant after three extractions.

Corrections have to be made for the increase in volume of the aqueous phase by solution of ether, and the ether and salts used have to be specially purified. If the acetate is difficult to obtain pure, accurate results can be obtained by using a solution of the sulphate or nitrate to which an equivalent quantity of sodium acetate has been added.

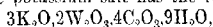
The determinations were carried out at  $18^{\circ}$ , the distribution coefficient of acetic acid between ether and water being taken as 2.1. The results obtained for percentage hydrolysis were as follows:  $N/2$ -cobalt acetate, 0.19;  $N/5$ , 0.165;  $N/2$ -nickel acetate, 0.435;  $N/5$ , 0.38. It follows that cobalt hydroxide is a stronger base than nickel hydroxide, and this agrees with the stabilities of their sulphates. The fact that the hydrolysis is greater in the stronger solutions may be due to the greater salting-out effect of the acetate on the acetic acid.

The hydrolysis of lanthanum acetate in  $N/5$ -solution was 0.315% and in  $N/10$ -solution 0.286%, the value 0.31% being taken as correct for both solutions, the differences being within the error of experiment. Lanthanum acetate was found to have  $1\frac{1}{2}H_2O$  of crystallisation, the solubility at  $18^{\circ}$  being 20.43 grams of the anhydrous salt in 100 grams of water; it loses  $\frac{1}{2}H_2O$  at  $100^{\circ}$ . T. S. P.

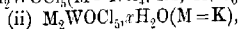
**A New Complex Form of Chromic Sulphate.** A. RECOURA (*Compt. rend.*, 1919, 169, 1163-1166).—When a  $N/2$ -solution of chromic sulphate is allowed to remain until equilibrium is reached, in so far as the formation of the green sulphate is concerned, and then evaporated to saturation point in a vacuum, on the addition of an excess of alcohol a lilac-grey precipitate is formed. If this precipitate is immediately collected and washed with a little ether, it is found to contain  $18H_2O$  and to have the whole of its  $SO_4$  precipitable by barium chloride. It changes, however, spontaneously and rapidly when exposed to the air, and at the end of the day contains only  $16H_2O$ , and gives no precipitate with barium chloride. If left in a desiccator, its water content finally drops to  $12H_2O$ . The constitution of this new complex sulphate has not yet been determined. W. G.

**Method of Obtaining, and Optical Study of, Crystals of Sodium Chromate Tetrahydrate.** LUCIEN DELHAYE (*Bull. Soc. franç. min.*, 1918, **41**, 80—92).—Deliquescent monoclinic crystals 5 mm. in length can be obtained by allowing a solution of sodium chromate saturated at 50° to cool to about 27°, filtering, and keeping for several days with occasional shaking. The refractive indices, optic axial angle, dispersion, etc., have been measured for light of various wave-lengths. CHEMICAL ABSTRACTS.

**Chemistry of Quinquevalent Tungsten.** OSCAR OSON COLLENBERG (*Arkiv. Kem. Min. Geol.*, 1918, **7**, No. 5, 1—35).—Solutions of tungstic acid and alkali tungstates in oxalic acid or alkali oxalate solutions are readily reduced to quinquevalent tungsten derivatives. From the solution of tungstic acid in oxalic acid, pure, solid reduction products could not be isolated, but if the solution is saturated with hydrogen chloride and then treated with a solution of rubidium chloride in concentrated hydrochloric acid, the compound *dirubidium pentachlorotungstite*,  $\text{Rb}_2\text{WOCl}_5$ , crystallises out in very good yield. When a solution of an alkali tungstate in oxalic acid solution containing a slight excess of alkali oxalate is reduced with tin foil, the colour passes through dark blue and becomes green, yellowish-green, and finally red. On cooling the highly concentrated solution, oxalic acid, alkali oxalate, and tin oxalate separate. The tin is removed by hydrogen sulphide from the solution, and, on adding alcohol, a dark reddish-brown powder separates. On dissolving the powder in water and adding an excess of alkali iodide or bromide, it is obtained pure. In this way, the *oxalo-tungstites* of sodium, potassium, and ammonium have been prepared. The potassium salt has the formula



whilst the sodium salt is similar, except that it contains  $12\text{H}_2\text{O}$ . The oxalo-tungstites are suitable substances for the preparation of other quinquevalent tungsten derivatives. They dissolve readily in hydrochloric acid to produce deep blue solutions, from which the oxy-chlorides of quinquevalent tungsten may be separated. They are soluble in potassium thiocyanate solution, producing deep red-coloured solutions; they dissolve in concentrated hydrofluoric acid solution, producing violet solutions. On boiling with potassium cyanide, yellow solutions are obtained, from which double cyanides of the type  $\text{M}_2\text{W}(\text{CN})_6$  may be isolated. The alkali oxalo-tungstites may be converted into chloro-tungstites by the following methods: (a) by treating the hydrochloric acid solution of an alkali (K or  $\text{NH}_4$ ) oxalo-tungstite with hydrogen chloride, (b) by adding chlorides (rubidium, caesium, aniline, tetraethylammonium, and tetrapropylammonium) to the hydrochloric acid solution of an oxalo-tungstite, and (c) by adding either pyridinium chloride or quinolinium chloride to a solution of ammonium chloro-tungstite in concentrated hydrochloric acid. By these methods, derivatives of the types: (i)  $\text{M}_2\text{WOCl}_5(\text{M} = \text{NH}_4, \text{Rb}, \text{Cs}, \text{C}_6\text{H}_5\text{NH}_2)$ ,





(iii)  $\text{MWOCl}_4$  ( $\text{M} = \text{C}_5\text{H}_5\text{NH}$ ,  $\text{C}_9\text{H}_7\text{NH}$ ), and (iv)  $\text{MWOCl}_4 \cdot \text{H}_2\text{O}$  ( $\text{M} = [\text{C}_2\text{H}_5]_4\text{N}$ ,  $[\text{C}_3\text{H}_7]_4\text{N}$ ), have been prepared. All the derivatives obtained have been shown by titration with potassium permanganate or by titration with iodine and arsenious acid to contain the tungsten in the quinquevalent condition. The *chloro-tungstites* are finely crystalline powders; they are quite stable in dry air, but at  $60\text{--}70^\circ$  are oxidised, turning blue, and eventually quite white. They are hydrolysed by water, and a reddish-brown hydroxide is produced. In the case of the less soluble compounds, for example, the caesium salt,  $\text{Cs}_2\text{WOCl}_5$ , the hydrolysis is not complete. The chloro-tungstites are soluble in concentrated hydrochloric acid, and in the case of the metal derivatives the solubility decreases with increasing atomic weight; they are insoluble in most organic solvents, except in the case of the rubidium and caesium derivatives, which are soluble in absolute methyl and ethyl alcohol. The solubility in methyl alcohol is very much greater than in ethyl alcohol. Oxidising agents convert the chloro-tungstites into sexavalent tungsten derivatives. A vigorous reaction takes place on treatment with potassium cyanide, with the production of double cyanides of the type  $\text{M}_4\text{W}(\text{CN})_8$ . The compounds of the type (iii) and (iv) are regarded as derivatives of metatungstous acid,  $\text{O}_2\text{W} \cdot \text{OH} \rightarrow \text{Cl}_4\text{W} \cdot \text{OH}$ , whilst those of types (i) and (ii) are regarded as derivatives of orthotungstous acid,  $\text{W}(\text{OH})_6 \rightarrow (\text{HO})_2\text{W}(\text{OH})_4 \rightarrow \text{HCl}_2 \cdot \text{WCl}_4$ . For the special description and preparation of the individual chloro-tungstites, the original should be consulted.

J. F. S.

**Decomposition of Stannous Chloride by Water and by Potassium Hydroxide Solutions.** C. M. CARSON (*J. Amer. Chem. Soc.*, 1919, **41**, 1969—1977).—Making use of the principles of the phase rule, the author has investigated the action of water and potassium hydroxide on stannous chloride. The experimental results show that the compound,  $2\text{SnCl}_4 \cdot 7\text{Sn}(\text{OH})_2$ , is the most basic of all the basic stannous chlorides. A slightly variable, crystalline material of approximately the formula  $3\text{SnCl}_4 \cdot 5\text{SnO}_3 \cdot 3\text{H}_2\text{O}$  is the precipitate commonly formed by the action of boiling potassium hydroxide on an excess of stannous chloride, and there is no compound of intermediate composition. Whether any basic compound lies between  $3\text{SnCl}_4 \cdot 5\text{SnO}_3 \cdot 3\text{H}_2\text{O}$  and the normal salt was not determined. The precipitates usually formed by the action of water on stannous chloride contain such a large proportion of stannic compound that the analyses are of no value in ascertaining the composition of the basic stannous chlorides.

J. F. S.

**The Peroxides of Bismuth.** RICHARD ROBERT LE GETT WORSLEY and PHILIP WILFRED ROBERTSON (*T.*, 1920, 117, 63—67).

**Behaviour of Hydrogen towards Rhodium.** A. GUTRIER and O. MAISCH (*Ber.*, 1919, **52**, [B], 2275—2280).—The experi-

ments were performed in the same manner as with palladium, iridium, and platinum (A., 1913, ii, 608; 1919, ii, 367, 368). The results may be summarised in the following manner. The deep black modification, rhodium-black, is able to absorb far more hydrogen than any other form. The maxima of hydrogen absorption amounted to 180 volumes at 190° for the greyish-black form, 165 volumes at 40° for the slightly greyish-black variety, and 206 volumes at 0° for the deep black modification. (The varieties are obtained in the order given by the reduction of sodium rhodium chloride by hydrazine in faintly acid, neutral and ammoniacal solution respectively; the purest preparations, dried in a vacuum over phosphoric oxide, contained about 3% of water and 0.3% of oxygen.) The absorption of hydrogen by rhodium is much less than by palladium, and corresponds with that observed with platinum. Spongy rhodium, like spongy platinum, only absorbs small amounts of hydrogen.

H. W.

### Mineralogical Chemistry.

#### Hausmannite in the Batesville District, Arkansas. H. D.

MISER and J. G. FAIRCHILD (*J. Washington Acad. Sci.*, 1920, 10, 1-8).—The abundant manganese ores of this district consist of the oxides psilomelane, hausmannite, braunite, manganite, pyrolusite, and wad, the first two, which occur intimately intergrown, being the commonest. They occur as irregular masses, weighing from less than a pound to 22 tons, embedded in clay, limestone, shale, sandstone, etc. The hausmannite, however, occurs as a replacement material only in the limestone, and as a residual material in clay derived from limestone. Analysis I is of a sample from the W. T. Gray mine near Pfeiffer, and II from Club House mine, near Cushman; they correspond with hausmannite ( $\text{Mn}_3\text{O}_4$ ) with 13% and 31% admixed psilomelane respectively.

	MnO.	O.	$\text{Fe}_2\text{O}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{SiO}_2$ .	CaO.
I .....	91.38	7.78	Nil.	Nil.	Nil.	Trace
II .....	90.40	8.87	0.48*		0.10	Trace
	MgO.	BaO.	$\text{H}_2\text{O}$ .	Total.	Sp. gr.	
I .....	Trace	0.26	0.62	100.04	4.836	
II .....	Trace	Nil.	1.03	100.88	4.778	

\*  $\text{Fe}_2\text{O}_3$  trace.

The 'braunite' described by Penrose in 1891 is shown to be such a mixture of hausmannite and psilomelane. Braunite is readily distinguished by the fact that it yields considerable gelatinous silica.

L. J. S.

**Analyses of Dolomites.** ALBERT ROTHROCK and J. B. SHUMAKER (*Chem. News*, 1920, **120**, 29—31).—The following analyses of dolomite rocks and dolomitic limestones from various localities show considerable variations from typical dolomite,  $\text{CaMg}(\text{CO}_3)_2$ , which contains  $\text{CaCO}_3$  54.35%,  $\text{MgCO}_3$  45.65%. I, white, compact, crystalline, from Ossining, New York. II, dark grey, massive, from Cumberland. III, light coloured, massive, from Cerro Gordo, Inyo Co., California. IV, grey, compact with conchoidal fracture, from Frankenstein, Silesia; this approaches magnesite. V, white, compact, and crystalline, resembling marble, from near Keeler, California. VI, greyish-white, crumbly, and saccharoidal, from the Binnenthal, Switzerland. VII, hard, compact, from Gerolstein, Rhine. VIII, light colour with pearly lustre, from Costa da Val, Tyrol;  $2\text{CaCO}_3, \text{MgCO}_3, \text{FeCO}_3$ . IX, greyish-white, compact, from New Almadin, California. X, light grey, granular, and porous, from Raible, Carinthia. XI, grey, large crystals, from Brewster's, New York. XII, *a*, outer layer of pale pink crystals, *b*, inner portion of dark grey crystals. XIII, grey from 'The Dolomites,' Tyrol. XIV, from the Brenner Pass.

	$\text{CaCO}_3$	$\text{MgCO}_3$	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	Total	Sp. gr.
I. ....	51.97	37.40	0.20	Trace	10.61	100.18	2.93
II. ....	57.59	24.98	16.05	0.87	0.56	100.05	2.88
III. ....	87.88	11.85	0.09	—	0.06	99.88	2.57
IV. ....	27.04	67.91	3.71	0.73	0.13	99.52	2.9
V. ....	66.08	1.15	0.06	—	32.57	99.86	2.7
VI. ....	49.00	40.23	0.48	—	10.84	100.55	2.85
VII. ....	52.93	44.33	0.80	0.22	1.23	99.51	2.82
VIII. ....	49.59	24.50	2.36	—	0.12	100.01*	3.01
IX. ....	53.28	45.18	8.57	—	0.4	100.11?	2.8
X. ....	54.64	45.18	Trace	0.28	0.23	100.33	2.7
XI. ....	59.98	36.83	2.44	—	0.33	99.58	2.9
XIIa. ....	56.63	41.37	1.18	0.63	0.23	100.04	—
XIIb. ....	57.18	36.83	0.89	1.16	3.96	100.02	—
XIII. ....	94.21	4.15	0.56	0.57	0.48	99.97	2.73
XIV. ....	96.25	2.98	0.50		0.35	100.08	—

\* Including  $\text{FeCO}_3$ , 23.44.

L. J. S.

### Analytical Chemistry.

**Application of the Interferometer to Gas Analysis.** J. D. EDWARDS (*Chem. and Met. Eng.*, 1919, **21**, 560—565).—The gas interferometer measures the difference in refractivity of two gases of binary mixtures. Usually, one of the components is taken as the standard gas, and the difference in refractivity of the mixture and one of its components is determined. For a change of  $\alpha\%$  of one of the components the change in refractivity

$$\Delta R = 273/T \cdot p/760 \cdot \alpha/100(R_1 - R_2).$$

Each scale division corresponds with a definite value of  $\Delta r$ , which is the difference in refraction of the two gases. The calibration of the instrument is described (see also A., 1918, ii, 47). In measuring a small percentage of a gas which deviates appreciably from Boyle's law, a correction is necessitated, as the refractivity of the gas at a low partial pressure differs from the value calculated from the pressure ratios.

In taking readings, calibration curves should be drawn for different temperature and pressure intervals from which readings may be taken by interpolation. A variation of  $3^\circ$  in the temperatures of estimation and of calibration involves an error of 1%. The error due to shifting of the central white or achromatic fringe was investigated by Adams (A., 1915, ii, 478).

Typical illustrations are given of the use of the instrument for air-carbon dioxide mixtures. It may also be employed for the analysis of flue gases and the determination of helium in mixtures.

A table is given showing the relative sensitiveness of the interferometer for different gases.

W. J. W.

**Improved Orsat Apparatus for Gas Analysis.** G. W. JONES and F. R. NEUMEISTER (*Chem. and Min. Eng.*, 1919, 21, 734—736).—The modification of Orsat's apparatus used by the Bureau of Mines, U.S.A., has a Jager's copper oxide tube for the removal of hydrogen and carbon monoxide. The gas burette can be put in communication either with the Orsat pipettes, containing the usual reagents for carbon dioxide, unsaturated hydrocarbons, and oxygen, or with a compensator of the Petersen type, the mercury in which forms contact with a platinum wire and lights a lamp, when the levelling bulb is raised or lowered, and thus facilitates the reading of the level. The copper oxide tube above the Orsat bulbs is heated by means of an electrical heater, which is lowered over it, and then rests on supports. For the determination of hydrocarbons in a gas, a combustion is made in the combustion pipette with a measured quantity of oxygen, the pipette being cooled by compressed air to prevent breakage, and the amounts of the two predominating hydrocarbons are calculated by means of the usual formulæ from the total contraction and amount of carbon dioxide found after the combustion. [See, further, *J. Soc. Chem. Ind.*, 1920, 138A.]

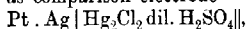
C. A. M.

**Theory of Electrometric Titration.** W. D. TREADWELL (*Helv. Chim. Acta*, 1919, 2, 672—680).—A theoretical paper in which the determination of the end-point in the titration of silver solutions is considered. The method consists in measuring the terminal voltage between a standard silver chloride cell and a silver electrode immersed in the solution, the end-point being that at which the voltage becomes zero. The theory is considered for the titration of solutions of pure silver salts and of the case where there is a quantity of other substances present.

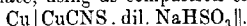
J. F. S.

**Electrometric Titration.** W. D. TREADWELL and L. WEISS (*Helv. Chim. Acta*, 1919, 2, 680—697).—It is shown that the end-

point of many titrations may be determined electrometrically by measuring the terminal voltage between a metal electrode, which is immersed in the solution being titrated, and is capable of sending the same ions into the solution, and a comparison electrode made of the same metal and the insoluble precipitate or product produced in the titration. The two terminals are directly connected with a voltmeter, and the point of zero potential is the end-point of the titration, that is, the point at which the concentration of the metal ions is the same in both the solution being titrated and the comparison electrode. It is essential that during the titration the liquid should be rapidly stirred, and the authors describe an apparatus in which the comparison electrode is built up in the stirrer. In the case of silver solutions, the comparison electrode is  $\text{Ag}|\text{AgCl sat.}|$ , a silver wire furnishes the electrode in the solution, and the titration is carried out with standard sodium chloride. The results are extraordinarily good. In the presence of foreign substances the titration values are too low, but they may be corrected from the course of the titration curve. Hydrogen sulphide may be titrated with silver ions, using as comparison electrode the combination  $\text{Ag}|\text{Ag}_2\text{S. dil. NaNO}_3||$ . Mercurous ions may be titrated by chloride ions, using as comparison electrode



and a similar silver-plated platinum wire as titration electrode. Better results are obtained if the titration is carried out with bromide ions and the calomel in the comparison electrode substituted by mercurous bromide. Copper ions may be titrated by ammonium thiocyanate, using as comparison electrode



In the foregoing cases soluble electrodes have been employed; further experiments were made with insoluble electrodes, and it is found that zinc ions may be titrated with ferrocyanide ion, using as titration electrode a platinum gauze and as comparison electrode  $\text{Pt}|\text{Zn}_2\text{Fe}(\text{CN})_6 \cdot \text{HCl}(5 \text{ c.c. in } 300\text{H}_2\text{O})||$ . The titration in this case is carried out at  $70^\circ$ . Ferrous chloride may be titrated with potassium dichromate, using an already completed titration as the comparison electrode and platinum wires in both solutions. This titration is also carried out in warm solutions. Uranous ions may be titrated with potassium permanganate in warm solution, using platinum wires and a uranyl solution as the comparison electrode. Vanadyl solutions may be similarly titrated with permanganate, using platinum wires and a vanadate solution as comparison electrode. In the case of the hydrogen-ion titration, the electrode is too slow in its action for the method as at present constituted to give sharp results.

J. F. S.

**Electrometric Titration.** J. PINKHORF (*Chem. Weekblad*, 1919, 16, 1163—1167).—The investigation concerned the selection of a constant electrode which should have the same potential as the electrode of the liquid at the moment when the end-point was reached. It would then be merely necessary to determine whether the difference of potential of the two electrodes was positive or nega-

tive. To ascertain which compensation electrode is suitable, a potential measurement was made during titration, and when the desired potential was found a combination of electrode and liquid was sought which would give this potential. For the titration of halogens in presence of each other, *N*-potassium bromide is suitable for the compensation electrode in the estimation of the iodine. For the bromine  $\text{Ag-AgCl-0.2NCl}$  is used. In titrating heavy metals with sodium sulphide, a silver-halogen compensation electrode is employed. Titrations of bases with mercuric oxide electrode and the use of the hydrogen electrode are discussed.

W. J. W.

**A Rapid Hydrogen Electrode Method for Determination of Hydrogen-ion Concentrations in Bacterial Cultures or in other Turbid or Coloured Fluids.** HARRY M. JONES (*J. Infect. Dis.*, 1919, 25, 262—268).—As compared with the colorimetric method, the apparatus described has wider application, is more accurate, less cumbersome, and only slightly less rapid. The hydrogen electrode vessel described was designed to provide a vessel accurate at least to 0.01  $p_H$  and to give a rapid saturation with hydrogen gas, and yet one which is easily constructed. A rapid and labour-saving technique combining the indicator and the gas-chain methods is described, which obviates the difficult task of preparing standard solution for the former method, and of making needless repetitions by the latter.

CHEMICAL ABSTRACTS.

**Iodometric Estimation of Acids.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, 57, 53—68).—The author has investigated the iodometric method, especially with reference to weak acids. The influence of dilution in the case of strong acids, of catalysts, and of a variation in the amount of potassium iodide added, was determined. Tests were carried out with hydrogen chloride, tartaric acid, citric acid, lactic acid, malic acid, succinic acid, acetic acid, formic acid, benzoic acid, salicylic acid, sodium phosphate, and currant juice. The iodometric method gives excellent results with strong acids, especially if diluted, in which case the reagents, after mixing, must remain for ten minutes before titration. A deficiency of potassium iodide causes inaccuracy. Organic oxy-acids can be accurately estimated if a salt of calcium, magnesium, or zinc is added. For phosphoric acid and weak organic acids, not containing a hydroxy-group, the method is unsuitable, but it may be used in the case of formic acid. The applicability of the method to the estimation of fruit juices requires further investigation.

W. J. W.

**Indirect Electrolytic Estimation of Anions without Platinum Electrodes. II.** E. LASALA (*Anal. Fis. Quim.*, 1919, 17, 235—247).—A continuation of work already published (*A.*, 1919, ii, 239). The present communication deals also with anions which form insoluble silver salts. These are carbonate, oxalate, ferro- and ferri-cyanide, orthophosphate, arsenate, chromate, and thiocyanate. The anion is precipitated as insoluble silver salt.

This is dissolved in a suitable solvent, and the silver estimated electrolytically with a nickel-plated copper cathode and an iron anode. Satisfactory results were obtained only in the case of carbonate, oxalate, ferro- and ferri-cyanide, and thiocyanate. The method was applied to the separation of chloride and iodide. The precipitated mixed silver haloid is washed with ammonia solution (D 0.92). The silver chloride is electrolysed after the addition of ammonium sulphate. The residual iodide is dissolved in 20% solution of potassium cyanide and electrolysed. A small correction must be applied for the solubility of silver iodide in ammonia solution. W. S. M.

**Electrolytic Estimation of the Halogens. An Indirect Method.** J. H. REEDY (*J. Amer. Chem. Soc.*, 1919, **41**, 1898—1902). —The decomposition voltage of *N*-sulphuric acid, saturated with silver chloride, between silver coated with silver chloride as anode and bright platinum as cathode is found to be 0.59 volt, which corresponds exactly with the sum of the solution potential of silver (0.52 volt) and the overvoltage of hydrogen on bright platinum (0.07 volt). As long as this limiting voltage of 0.59 volt is not exceeded, the electrolysis of haloid solutions with silver anodes proceeds with the formation of an adherent layer of silver haloid on the anode without precipitation in the solution. With the completion of the deposition of the halogen, silver ions appear in the solution with no break in the continuity of the current and with scarcely any rise in potential. An indirect method of estimation of chlorides, bromides, and iodides is based on the above facts. The principle of the method consists in depositing the halogen on a silver anode under a constant voltage of 0.59 volt; some silver will thereby be lost from the anode. The anode is then dried and weighed, and the silver haloid is reduced to metallic silver and the loss in weight determined, which gives the weight of the halogen. A lead accumulator of large capacity is connected across the ends of a sliding rheostat and a current of *E.M.F.* 0.59 volt tapped off. The electrolysis vessel consists of a beaker of 400 c.c. capacity fitted with an anode of silver gauze, coated with silver electrolytically, and a bright platinum cathode and a stirrer. The electrolysis is carried out with 200 c.c. of solution for about fifteen minutes; the current flowing at first is rather large, but after about fifteen minutes it becomes negligible. The potential is then raised to 0.60 volt for five minutes. The silver electrode with its halogen deposit is washed, dried, and weighed. After weighing, it is made the cathode in a dilute solution of sodium hydroxide and electrolysis carried out until hydrogen is freely liberated from the surface. The silver haloid is thus reduced to black silver, which is not very adherent and must be carefully handled. After a thorough washing, the electrode is heated at 500° in an electric furnace until the deposit is white, and thoroughly sintered together. It is then weighed, and the loss in weight gives the weight of the halogen. The results given in the paper show that the method is quite as good as the usual gravimetric method.

J. F. S.

**Estimation of Bromide in Mineral Waters and Brines.**

W. W. SKINNER and W. F. BAUGHMAN (*Science*, 1919, **50**, 50).—Chromic acid in concentrated solution liberates bromine quantitatively from bromides at the ordinary temperature, and the bromine is removed by aspiration. Only a trace of chlorine is liberated from chlorides. When chromic acid acts on a solution containing chloride and bromide, therefore, the mixture of halogens removed by aspiration is dissolved in a solution of sodium sulphite and hydroxide, which is then evaporated to dryness and the residue again treated with chromic acid solution and aspirated a second time. The double treatment gives very trustworthy results.

## CHEMICAL ABSTRACTS.

**Estimation of Alkali Sulphide in Dilute Solution.** H. G.

BENNETT and W. G. BENNETT (*J. Soc. Leather Trades Chem.*, 1919, **3**, (11), 190—193).—A measured quantity of the solution containing not more than 0.04% of hydrogen sulphide is distilled in an atmosphere of carbon dioxide with an excess of boiling magnesium chloride solution. A current of carbon dioxide carries the liberated hydrogen sulphide into a receiver containing standard iodine solution. A second receiver, containing standard sodium arsenite solution, is arranged to trap any iodine vapour carried over by the gas. The method is accurate under these conditions and provided there are no rubber connections exposed to the iodine vapour. D. W.

**Neutralisation Curve of Sulphurous Acid.** I. M. KOLTHOFF

(*Chem. Weekblad*, 1919, **16**, 1154—1163).—The accuracy of the results when sulphurous acid is titrated with methyl-orange or dimethyl-yellow as indicator depends on the concentration of the hydrogen ions of the sodium hydrogen sulphite, and therefore also on the second dissociation constant of the sulphurous acid. This has been determined from the degree of hydrolysis of solutions of sodium sulphite and found to be  $1 \times 10^{-7}$  at 15°. The hydrogen-ions concentration of a 0.1 mol. sodium hydrogen sulphite solution calculated from the two dissociation constants gave the value  $[H^+] = 3.3 \times 10^{-5}$ . A curve showing the neutralisation of sulphurous acid was constructed. In the titration of sulphurous acid errors of  $\pm 2\%$  and of  $\pm 6\%$  were obtained when the indicators were dimethyl-yellow and phenolphthalein respectively. The addition of sodium chloride reduced the error with phenolphthalein to  $\pm 2\%$ . Accuracy can only be ensured if excess of barium nitrate is added after the pink coloration of the phenolphthalein has appeared, and the titration then continued to the end-point. W. J. W.

**Estimation of Sulphates in the presence of Organic Sulphonic Acids.** T. CALLAN, JAS. A. RUSSELL HENDERSON, and

R. BARTON (*J. Soc. Chem. Ind.*, 1919, **38**, 410—411).—The solution of the substance (containing about 0.2 gram of sulphate) is rendered slightly ammoniacal (a small quantity of calcium chloride is also added to precipitate any carbonate, which is then separated by filtration), and the mixture is boiled until all excess of ammonia



has been expelled. Twenty c.c. of  $N/4$ -barium chloride solution are then added, the heating continued for a few minutes, and the excess of barium titrated with  $N/4$ -potassium chromate solution, using starch-iodide paper as indicator. A drop of the mixture is placed on the paper, and the edge of the spot is touched with a drop of very dilute hydrochloric acid. A blue colour develops in about ten seconds when an excess of soluble chromate is present. An immediate blue colour indicates that a considerable excess of chromate has been added.

W. P. S.

**Detection of Nitrogen in Organic Compounds by Castellana's Reaction.** J. FLIERINGA (*Pharm. Weekblad*, 1920, 57, 3—4).—Castellana's reaction (A., 1905, ii, 207) may give a positive reaction even in nitrogen-free compounds, owing to combination of atmospheric nitrogen, if the magnesium is in excess. It is preferable to use a mixture of 2 parts of sodium carbonate and 1 part of magnesium. Sodium carbonate containing 1 molecule of  $H_2O$  should be employed. Addition of sugar to the reaction mixture eliminates the error caused by absorption of atmospheric nitrogen.

W. J. W.

**The Relative Accuracy of Colorimetric and Titrimetric Procedures for estimating Nitrogen as Ammonia.** E. R. ALLEN and B. S. DAVISSON (*J. Biol. Chem.*, 1919, 40, 183—197).—It appears that the colorimetric methods are slightly the more accurate. On the other hand, the conditions for accurate titrations may be attained more easily than those for satisfactory Nessler estimations, and at the same time the titrimetric methods are applicable to a wide range of nitrogen values. The chief disadvantage of the Nessler process is the fact that the reaction is imperfectly understood, and the appearance of clouds and precipitates difficult to avoid. Again, it is believed that the personal error is greater in colorimetric methods than in titrimetric methods. The general conclusion is therefore in favour of the titrimetric methods.

J. C. D.

**Estimation of Nitrogen in Nitrates.** F. PILZ (*Zeitsch. landw. Vers.-Wesen Deutschösterreich*, 1919, 22, 180—188; from *Chem. Zentr.*, 1919, iv, 767).—Comparative estimations of nitrogen in nitrates by various methods showed that reduction with Devarda's alloy yielded the most trustworthy results, and is to be recommended more than the method described by Arnd (A., 1917, ii, 504). Busch's method (A., 1905, ii, 418) is less trustworthy. Other methods investigated were the one proposed by Ulsch (reduction in acid solution with iron powder) and the indirect method (conversion of the nitrate into chloride).

W. P. S.

**Method for the Estimation of Minute Quantities of Nitrogen in Organic Substances, which furnishes a New Quantitative Method of Diagnosis in some cases of Mental Disease.** R. V. STANFORD (*Rep. Chem. Lab. Cardiff City Mental Hosp.*, 1919, No. 2. Compare A., 1913, i, 930).—A small quantity

of the organic substance, as, for example, 1 c.c. of cerebrospinal fluid, is oxidised by the Kjeldahl process in the usual manner. The subsequent distillation is carried out in the ordinary apparatus, but the distillate is collected in three fractions in Nessler cylinders. The third fraction should show little or no coloration with Nessler's reagent. The colour produced by the first two fractions is compared in the usual manner with that produced by a standard solution of ammonium chloride. Considerable care has to be taken to avoid errors arising from ammonia in the reagents and apparatus.

The author records a number of analyses of cerebrospinal fluid from mental cases. The "nitrogen number," that is, the number of hundredths of a milligram of total nitrogen contained in 1 c.c. of cerebrospinal fluid, may be of value in diagnosis. On the whole, density and nitrogen number of the fluids run parallel to one another.

No traces of choline and only the merest traces of ammonium salt were detected in the cerebrospinal fluid in mental disease.

J. C. D.

**Process for the Estimation of Arsenic. Chemistry of the Marsh-Berzelius Process.** B. S. EVANS (*Analyst*, 1920, 45, 8—17).—The arsenic is evolved as hydrogen arsenide, in the same

way as in the ordinary Marsh-Berzelius test, but is conducted over a roll of red-hot copper, which retains the arsenic, the amount of which is obtained from the increased weight of the copper. The compound formed with the copper usually melts and resembles solder in appearance, but occasionally brilliant, silvery-white, blade-shaped crystals are produced. Analyses of the deposits gave 67.5 and 70.5% of copper and 32.28 and 29.27% of arsenic, and thus appeared to be mixtures of the arsenides  $\text{Cu}_3\text{As}$  and  $\text{Cu}_5\text{As}_2$ . The results obtained with elementary arsenic and various arsenic compounds were invariably 1.4% too low, and the cause of this loss could not be definitely traced, although the results indicated that if the arsenic remained in the flask, it was in the form of a very stable complex. In order to prevent separation of elementary arsenic, it is advisable that the amount of substance introduced should contain considerably less than 0.5 gram of arsenic. [See also *J. Soc. Chem. Ind.*, 1920, February.] C. A. M.

**Estimation of Arsenic in Tin and Tinnings.** LUCIEN VALLERY (*Compt. rend.*, 1919, 169, 1400—1402).—Marsh's method is liable to give results which may, in some cases, be wrong to the extent of 75% of the amount found when applied to the estimation of arsenic in tin. The author recommends that the arsenic should be distilled off as arsenic chloride by Hollard and Bertiaux's method, and the arsenic estimated colorimetrically in the distillate after reduction to colloidal arsenic by means of hypophosphorous acid. In this way, the results obtained are accurate to within 3% of the total at a concentration of 1 in 100,000. W. G.

**New Method of Estimation of Carbon and Hydrogen in Organic Substances.** KUNIHICO SUMIKURA (*J. Tokyo Chem. Soc.*, 1919, 40, 593—606).—The essential point of the method is the combined use of platinum and cerium dioxide. (1) *Substances containing Carbon, Hydrogen (and Oxygen) only.*—An ordinary combustion tube is filled, in order, with cerium dioxide (5 cm.), porcelain boat, cerium dioxide (8 cm.) (only one burner is necessary under each of these), and a coil of platinum or platinum-iridium wire (2 m.), which is electrically heated with adjustable resistances. The wire is first heated in a separate tube before being placed in the combustion tube. The cerium dioxide is prepared by heating copper gauze packed with asbestos soaked in a solution of ceric nitrate.

(2) *Substances containing Nitrogen and Sulphur.*—Lead dioxide is placed between the second cerium dioxide gauze and the platinum coil, and is heated at 300—350°. (3) *Substances containing Halogens.*—Silver foil is placed between the second cerium dioxide gauze and the platinum wire. If nitrogen is also present, lead dioxide is placed between the silver foil and the platinum wire, and is heated at 300—320°. (4) *Substances containing Phosphorus.*—Lead monoxide is mixed with the substance. Trustworthy results are recorded.

CHEMICAL ABSTRACTS.

**Rapid Estimation of Carbon Monoxide in Air.** ARTHUR B. LAMB and ALFRED T. LARSON (*J. Amer. Chem. Soc.*, 1919, 41, 1908—1920).—Two methods for the rapid estimation of small quantities of carbon monoxide in air are described. In the first method, the gas is passed over a platinum wire heated to redness, and the carbon monoxide partly burned in contact with it. The gas then passes over heated copper oxide, where the carbon monoxide is completely burnt; it then passes through a spiral contained in a thermostat to bring it to its original temperature, and finally over a second exactly similar platinum wire heated by the same current as the first. The two platinum wires are made arms of a Wheatstone bridge, and since the first wire will necessarily be hotter than the second, they will have different resistances. The change in the resistance of the first wire gives a measure of the carbon monoxide concentration. In the second method, the mixture is passed through a platinised platinum catalyst, when the carbon monoxide is completely burnt. The temperature change is measured by a thermo-element, and indicates the concentration of carbon monoxide. Both methods are rapid, and the latter is particularly accurate, easy to instal and to operate. The catalyst, with reasonable precautions, remains active for many weeks.

J. F. S.

**Apparatus for the Volumetric Estimation of Small Quantities of Carbon Dioxide by Displacement from Liquids by means of a Rapid Current of Air at the Ordinary Temperature and Pressure.** A. COSTANTINO (*Atti R. Accad. Lincei*, 1919, [v], 28, ii, 118—121).—In the apparatus described, which

consists of a closed system, a rotary mineral oil pump causes the repeated circulation of purified air, first through the liquid containing the carbon dioxide, and then through a definite volume of standard barium hydroxide solution, this being subsequently titrated with acid in presence of phenolphthalein. The determination occupies in all about forty-five minutes. Test experiments with sodium carbonate solutions containing 6.4–21 mg. of carbon dioxide show that the method yields accurate results. T. H. P.

**Estimation of Metals by Electrolytic Deposition without using an External Supply of Electricity.** MAURICE FRANÇOIS (*Ann. Chim.*, 1919, [ix], 12, 178–192).—A more detailed account of work already published (see A., 1919, ii, 34). W. G.

**Use of Nickel Crucibles for the J. Lawrence Smith Method in Estimating Soil Potassium.** SETH S. WALKER (*J. Ind. Eng. Chem.*, 1919, 11, 1139–1140).—The same results are obtained whether platinum or nickel crucibles are used for the heating of the soil with ammonium chloride and calcium carbonate, but the nickel crucible is attacked by the mixture and the life of the crucible is short. W. P. S.

**The McCrudden Gravimetric Calcium Method Modified.** J. P. HALVERSON and J. A. SCHULZ (*J. Ind. Eng. Chem.*, 1920, 12, 77–78).—The calcium oxalate precipitate is collected on a filter of specially prepared asbestos contained in a Gooch crucible; after washing, both filter and precipitate are mixed with water, acidified with sulphuric acid, and titrated at 65° with permanganate solution. The filter is prepared by digesting ignited asbestos with dilute sulphuric acid and a slight excess of permanganate for one hour at 60° to 70°, and then washing it until free from acid. [See, further, *J. Soc. Chem. Ind.*, 1920, February.] W. P. S.

**Estimation of the Calcium Oxide Content of Milk of Lime.** GEORG LENART (*Zeitsch. Ver. deut. Zuckerind.*, 1919, 1–15, 360–361).—Mategrák's table (*Österr.-Ungar. Zeitsch. Zuckerind.*, 1871, 12, 718) correlating the sp. gr. and calcium oxide content of milk of lime is regarded as far from correct, whilst that published by Lunge and Blattner (*Dingl. Polytechn. J.*, 1883, 466) is also considered to be untrustworthy. Experiments are described demonstrating the difficulty of obtaining exact results by means of the hydrometer (the method of density determination adopted in the construction of the second table), since the readings are influenced by the shape and length of the spindle, by the width and depth of the column of liquid in the cylinder, and also by the degree of movement imparted to the liquid at the moment of observation. Using a pycnometer consisting simply of a cylindrical vessel having a capacity of about 500 c.c., provided with a ground-glass plate as cover, a new table has been constructed by the author in which the density values range from 1.0085 to 1.2195 (1.5° to 26.2° B<sub>6</sub>.)

at 20°, temperature corrections being stated for readings made between 20° and 40°. Milk of lime which has been vigorously shaken for about two hours assumes a viscous condition, in which the particles remain almost completely in suspension for some days, this being believed to be due to the formation of a hydrated compound, probably  $\text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , to which attention has already been directed by Herzfeld (*Zeitsch. Ver. deut. Zuckerind.*, 1897, 817) and by Karcz (*Chem. Zeit.*, 1898, 22, 38). J. P. O.

**The Permanganate Method for Copper.** LOUIS F. CLARK (*J. Ind. Eng. Chem.*, 1919, 11, 1138—1139).—A modification of the procedure for the titration of cuprous thiocyanate with permanganate solution is proposed, with the object of making the estimation less arbitrary. The cuprous thiocyanate precipitate is treated in a beaker with 25 c.c. of hot 4% sodium hydroxide solution until the precipitate is decomposed, 25 c.c. of cold 15% sulphuric acid and a quantity of 1% ferric sulphate (anhydrous salt) solution are added, and the mixture is titrated with permanganate solution. Towards the end of the titration, and when the mixture becomes whiter in colour, 5 c.c. of concentrated hydrochloric acid are added, and the titration then completed. Under these conditions, 6 atoms of copper should be equivalent to 7 atoms of iron, or a ratio factor of 0.1626; the ratio factor actually found as the result of experiment is 0.1646. [See, further, *J. Soc. Chem. Ind.*, 1920, 138A.] W. P. S.

**Microchemical Identification of Soluble and Insoluble Mercury Compounds.** G. DENIGES (*Bull. Soc. Pharm. Bordeaux*, 1919; from *Ann. Chim. anal.*, 1919, [ii], 1, 383—385).—The tests depend on the characteristic crystals obtained when a small quantity of the compound is treated with a drop of potassium bromide-iodide solution. Mercurous compounds and mercuric cyanide are oxidised previously with bromine. Mercuric iodide itself is identified by the crystals obtained from its alcohol or acetone solution. W. P. S.

**Volumetric Estimation of Mercuric Chloride.** ORTO SASSE (*Pharm. Zeit.*, 1919, 64, 633).—Referring to the method described by Utz (A., 1919, ii, 428), the author mentions that he himself had published a method (*Pharm. Zeit.*, 1887) for the volumetric estimation of mercuric chloride; this method depends on a titration with potassium iodide solution, and is trustworthy. W. P. S.

**Application of Rotating Reductors in the Estimation of Iron.** WALTER SCOTT (*J. Ind. Eng. Chem.*, 1919, 11, 1135—1137).—Gooch and the author have shown previously (A., 1918, ii, 373) that vanadic acid may be reduced by rapidly rotating anodes of silver or copper, and the author now describes a similar method of reduction for ferric salts. The latter in sulphuric acid solution are reduced completely by rotating reductors of zinc or aluminium, with or without the use of an external current. W. P. S.

**A Sensitive Reaction for Manganese.** P. H. HERMANS (*Pharm. Weekblad*, 1919, 56, 1344—1346).—Caron and Raquet's reaction for manganese (*Rép. Pharm.*, 1919, 97) was independently discovered by the author, and was, in addition, utilised as a test for nitrogen tetroxide and for nitrites. All oxidising agents are not effective in promoting the red coloration, for example, hydrogen peroxide, potassium persulphate, chlorine, bromine, iodine, chloric acid, iodic acid, potassium ferricyanide, but addition to them of 0.5% solution of osmic acid produces a satisfactory result. Active oxidising agents for the test are bleaching powder, potassium permanganate, and dichromate, lead peroxide, cerium ammonium nitrate, nitrous acid, and nitrogen tetroxide.

Lead peroxide is most suitable for the manganese test. The reaction is sensitive to 0.07 mg. manganese or 0.03 mg. sodium nitrite per c.c. of solution.

The red coloration is considered to be a complex alkali manganese oxalate.

W. J. W.

**Indirect Detection of Tin.** FR. FEIGL (*Chem. Zeit.*, 1919, 43, 861).—Ferrous salts give a red precipitate with an ammoniacal solution of dimethylglyoxime, but the presence of ferric salts, which give a precipitate of ferric hydroxide with the reagent, interferes with the test. The precipitation of ferric iron as hydroxide and of ferrous iron as ferrous dimethylglyoxime may be prevented by adding an organic hydroxylated compound, such as citric or tartaric acids or potassium sodium tartrate, and the ferrous ion then gives a carmine-red solution. In each case, complex iron compounds are formed. In using this reaction as a sensitive indirect test for tin, the mixed sulphides, presumably of antimony and tin, are dissolved in hydrochloric acid, and one portion of the solution is tested for antimony with iron wire. In a second portion, the tin and antimony are precipitated by means of pure zinc, and the tin extracted from the deposit by means of concentrated hydrochloric acid. The solution is poured into a hot dilute solution of ferric chloride, a little citric acid or potassium sodium tartrate added, and the liquid tested with ammoniacal alcoholic dimethylglyoxime solution. The ferrous ion formed by reduction with the stannous ion will give a red coloration, the intensity of which is proportional to the amount of stannous chloride.

C. A. M.

**Estimation of Thiophen in Industrial Benzenes.** ANDRÉ MEYER (*Compt. rend.*, 1919, 169, 1402—1404).—A modification of Denigès's method (compare A., 1895, ii, 332, 372). Denigès's reagent is prepared by dissolving 50 grams of mercuric oxide in 200 c.c. of sulphuric acid diluted with 1000 c.c. of water. Twenty c.c. of this reagent are mixed with 75 c.c. of methyl alcohol and 5 c.c. of the benzene under examination in a stoppered bottle. The mixture is shaken from time to time, and, after thirty minutes, is filtered. Ten c.c. of the filtrate are diluted with 20 c.c. of water, a few drops of nitric acid are added, and the whole is titrated with

N/10-ammonium thiocyanate solution, using 1 c.c. of a 20% iron ammonium alum solution as indicator. In view of the possible presence of acetone in the methyl alcohol, a blank experiment is conducted, using pure benzene free from thiophen. The difference between the two titrations is a measure of the mercury precipitated by the thiophen as the compound,  $(\text{HgO})_2\text{SO}_4 \cdot \text{HgSC}_4\text{H}_7$ , and the factor for the conversion of mercury to thiophen is 0.14. W. G.

**Titration and Partial Reduction of Nitro-compounds with Titanous Chloride.** C. F. VAN DUIN (*Chem. Weekblad*, 1919, 16, 1111—1122).—An examination of the titanous chloride method for the titration of nitro-compounds. The constancy of titre of a titanous chloride solution at the ordinary temperatures and after heating was especially investigated; also the general applicability of the method to various classes of nitro-compounds. At the ordinary temperatures, only slight variations in titre were found after keeping for several days. Titration experiments before and after heating the titanous chloride solution were carried out in comparable conditions in presence of alcohol, hydrochloric acid, and acetic acid. It was found that the assumption of an invariable titre during the heating of the titanous chloride solution led to quite erroneous results. The error is small in presence of acids, especially in hydrochloric acid, tolerable results being only obtained in strongly acid solutions. From experiments with picric acid, *m*-dinitrobenzene, and *s*-trinitrotoluene, the author concludes that the method yields results of the same order of accuracy as the Dumas method. The reduction and titration of the following classes of nitro-compounds were carried out: nitroamines (*s*-trinitrophenylmethylnitroamine, aminotrinitrophenylmethylnitroamine, trinitromethylnitroaminophenol, trinitromethylnitroaminoanisole, trinitrodimethyldinitroaminobenzene), tetranitro-compounds (tetranitrophenol, tetranitrophenylmethylnitroamine, tetranitroaniline), and hexanitro-compounds with two nuclei (hexanitrodiphenyl sulphide, hexanitrodiphenylsulphone). In the reduction of nitroamines, side reactions may take place in which the nitroamino-group is entirely removed from the nucleus. In all cases, blank experiments must be carried out in order to estimate the alteration in the titanous chloride solution on heating. The amount of excess of the solution necessary for complete reduction must also be determined in each case. Only in those conditions can this method of nitrogen analysis be considered superior to that of Dumas.

W. S. M.

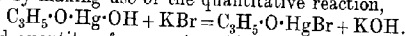
**Detection of Methyl Alcohol in Ethyl Alcohol.** M. POLINSKI (*Chem. Analyst*, 1919, 28, 11).—Five c.c. of the sample are distilled with 50 c.c. of water and 3 grams of sodium persulphate, the distillate being collected in fractions of 2 c.c. each. The fifth fraction is treated with eight drops of a freshly prepared, filtered 1% solution of phenylhydrazine hydrochloride, four drops of 5%

potassium ferrocyanide, and 1 c.c. of concentrated hydrochloric acid. A pink coloration is produced if methyl alcohol is present.

CHEMICAL ABSTRACTS.

**Complex Organic Mercury Compounds.** EINAR BILLMANN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, 5, No. 12, 1—11). —The complex compound formed from allyl alcohol and mercuric acetate is very stable, the concentration of the mercuric ion in a 1/160-molar solution being only  $10^{-8.40}$  (compare A., 1917, i, 123). This fact can be made use of in the electrometric estimation of allyl alcohol. The aqueous solution of allyl alcohol is put in a beaker containing mercury, which forms one electrode, the other being a calomel electrode. A standard solution of mercuric acetate is then run in, and the *E.M.F.* curve plotted. The point of inflexion on the curve is very sharp, and accurate results are obtained.

Allyl alcohol can also be estimated by adding mercuric acetate and potassium bromide to the solution, and titrating the acetic acid set free, with phenolphthalein as indicator. The liberation of acetic acid is quantitative, according to the equations:  $C_3H_5 \cdot OH + Hg(OAc)_2 = C_3H_5 \cdot O \cdot Hg \cdot OAc + AcOH$ ;  $C_3H_5 \cdot O \cdot Hg \cdot OAc + KBr = C_3H_5 \cdot O \cdot HgBr + OAcK$ . Mercury can also be estimated very accurately by making use of the quantitative reaction,



A weighed quantity of mercuric oxide is dissolved in 5*N*-sulphuric or nitric acid; the solution is diluted with water free from carbon dioxide, a few c.c. of allyl alcohol added, and then *N*/5-sodium hydroxide until the liquid is alkaline to phenolphthalein. The whole is then exactly neutralised with *N*/5-sulphuric acid, 5 grams of potassium bromide added, and the liquid well shaken to give a solution, the entrance of carbon dioxide being carefully excluded. The liberated alkali is then titrated. Halogen acids must not be present in estimations according to this method.

Maleic and crotonic acids do not give sufficiently stable complexes for estimation by the above methods, but *allocinnamic* acid gives good results with the mercuric acetate-potassium bromide method. Cinnamic acid also gives mercury complexes, and is to be reported on later.

Mercury can be readily and accurately estimated by a modification of Incze's method (A., 1917, ii, 327). To the solution of the mercuric salt, or of mercuric oxide in nitric or sulphuric acid, is added a large excess of alkali; the whole is then exactly neutralised with standard acid, using phenolphthalein as indicator. Potassium iodide (5 grams) is then added, and the liberated alkali carefully titrated, carbon dioxide being excluded. T. S. P.

**Titration of Organic Acids in Urine.** D. D. VAN SLYKE and W. W. PALMER (*Proc. Soc. Exp. Biol. Med.*, 1919, 16, 140—141). —Carbonates and phosphates are removed by adding 2 grams of calcium hydroxide to 100 c.c. of urine and filtering after ten minutes. The acidity of 25 c.c. of the filtrate is brought to  $p_H = 8$



(circa) by adding 0.2*N*-hydrochloric acid until the pink colour of phenolphthalein disappears, 5 c.c. of 0.02% Tropaeolin OO are added, and the solution is titrated to  $p_H=2.7$  with 0.2*N*-hydrochloric acid, the volume being brought to approximately 50 c.c. by the addition of water towards the end of the titration. The colour is compared with that of 50 c.c. of a control solution with the same  $p_H$  value and indicator. The amount of 0.2*N*-hydrochloric acid required to give the end-point with a control in which water replaces urine is subtracted. The titration estimates from 93% to 100% of each of the organic acids known to be present in urine in quantitatively significant amounts. It also includes very weak bases, but of this class of substances only creatine and creatinine, which are estimated to nearly 100%, are significant. The titration figure, corrected for the amounts of these two bases, represents the organic acids in urine. CHEMICAL ABSTRACTS.

**Detection of  $\beta$ -Hydroxybutyric Acid, Acetoacetic Acid, and Acetone in Urine.** R. LILLIG (*Pharm. Zeit.*, 1919, 64, 696—697, 707—709).—A collection of some sixty methods which have been proposed for the purpose; a brief description is given of each method. W. P. S.

**Bellier's Reaction for Vegetable Oils.** A. VAN RAALTE (*Chem. Weekblad*, 1919, 16, 959—960).—The benzene used for this reagent must be free from thiophen, otherwise a dirty green, instead of a violet, coloration is obtained. W. J. W.

**Relative Sensitiveness of the Fehling, Phenylhydrazine, and Nylander Tests for the Detection of Dextrose in Urine.** GEORGE E. EWE (*Amer. J. Pharm.*, 1919, 91, 717—719).—Fehling's test is the most sensitive of the three tests investigated; it yields a reaction with a solution containing 0.00125% of dextrose. The phenylhydrazine test is also sensitive, giving a reaction, after two hours, with a 0.0025% solution of dextrose, but the Nylander reagent (potassium sodium tartrate, 4 grams; 10% sodium hydroxide solution, 100 c.c.; bismuth subnitrate, 2 grams) fails to give a reaction unless the solution contains at least 0.5% of dextrose. W. P. S.

**Titration of Sugars.** E. SCHWALTER (*Zeitsch. Nahr. Genussm.*, 1919, 38, 221—227).—A reply to Rupp and Lehmann (*A.*, 1919, ii, 434); the author maintains the correctness of his former remarks (*A.*, 1919, ii, 172). W. P. S.

**The Isaacson Method for Estimating Dextrose.** ELISABETTA C. PENNELL (*J. Lab. Clin. Med.*, 1919, 4, 736—737).—Isaacson's method (*A.*, 1918, ii, 246) was found highly untrustworthy when compared with the Fehling volumetric method. CHEMICAL ABSTRACTS.

**Separation of Dextrose and Lævulose.** FRANZ LUCIUS (*Zeitsch. Nahr. Genussm.*, 1919, 38, 177—185).—A method for the estimation of dextrose in the presence of lævulose depends on the fact that the rotation of the latter is destroyed by heating for seven

hours with dilute hydrochloric acid, whilst that of dextrose is not affected. Fifty c.c. of the sugar solution (containing from 2 to 4% of the sugars) are mixed with 10 c.c. of 5*N*-hydrochloric acid and heated in a boiling water-bath for seven hours. The mixture is then nearly neutralised with sodium hydroxide solution, diluted to 100 c.c., treated with animal charcoal and filtered, if necessary, and polarised at 20°. About 99% of the dextrose actually present is found. The dextrose remaining after the acid treatment cannot be estimated by determining the copper-reducing power of the solution as the laevulose is converted into reducing substances, which, however, are optically inactive.

W. P. S.

**Separation of "Saccharin" from Benzoic Acid.** E. SCHOWALTER (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 185—194).—The presence of "saccharin" interferes with the estimation of benzoic acid in foods, etc., by the methods described by Mohler, von der Heide, and Grossfeld (A., 1908, ii, 906; 1910, ii, 359; 1915, ii, 848), but the two substances may be separated from one another by taking advantage of the insolubility of "saccharin" in carbon tetrachloride. The residue obtained on evaporating the ethereal solution of the two substances at a low temperature is dried under reduced pressure to remove the last traces of ether and acetic acid, and is then treated with carbon tetrachloride; the benzoic acid dissolved by this solvent may be estimated by titration and the insoluble "saccharin" identified by Klostermann and Scholta's reaction (A., 1916, ii, 586). Separation of the two substances between sublimation is untrustworthy; "saccharin" begins to sublime at 120° and 130°. Animal charcoal absorbs considerable quantities of "saccharin," its anhydride and sodium salt, as well as benzoic acid and benzoates, from an aqueous solution.

W. P. S.

**Estimation of *p*-Phenylenediamine.** T. CALLAN and JAS. A. RUSSELL HENDERSON (*J. Soc. Chem. Ind.*, 1919, **38**, 408—410).—A modification of a method described by Efront (A., 1905, ii, 60) is recommended. Fifty c.c. of sodium hypochlorite solution, containing 12—15% of available chlorine, are diluted to 1 litre, and 100 c.c. of this solution are diluted with an equal volume of water, 1 gram of sodium carbonate is added, followed by 10 c.c. of the *p*-phenylenediamine solution (in dilute hydrochloric acid); the latter solution should contain from 2 to 6% of the substance, and the addition should be made gradually with constant stirring. Benzoquinonedichloroimide is precipitated as a white substance and, without filtration, the excess of chlorine in the mixture is titrated with *N*/10-sodium arsenite solution. The difference between this titration and the quantity of arsenite solution required for the titration of the hypochlorite solution itself is equivalent to the amount of chlorine removed from solution as dichloroimide; 1 c.c. of *N*/10-arsenite solution therefore corresponds with 0.0018 gram of *p*-phenylenediamine. The method may also be used for the estimation of *p*-nitroaniline, *p*-aminodiphenylamine, benzidine, and naphthylene-1:4-diamine, but with the latter the yield found is

only 98—99% of the quantity of substance present owing to the slight solubility of the dichloroimide formed. The method is not applicable to substances containing a sulphonic group, since these give soluble dichloroimides.

W. P. S.

**Estimation of Carbamide in Blood and Urine.** H. CITRON (*Deut. med. Woch.*, 1919, **45**, 975; from *Chem. Zentr.*, 1919, iv, 719).—A reply to Brahm (this vol., ii, 66).

H. W.

**Electrometric Method for the Estimation of Ferrocyanides depending on a Change in Oxidation Potential.** G. L.

KELLEY and R. T. BOHN (*J. Amer. Chem. Soc.*, 1919, **41**, 1776—1783).—Solutions of ferrocyanides may be estimated by titration with potassium permanganate in the presence of sulphuric acid, using the sudden change in *E.M.F.* observed with a bright platinum electrode to mark the end-point. The method is as follows: About 1 gram of potassium ferrocyanide in 250 c.c. of water and 2.5—5.0 c.c. of sulphuric acid (*D* 1.58) is titrated with 0.05*N* potassium permanganate, using an electrometric apparatus which will indicate changes of potential of the order of one millivolt (A., 1917, ii, 512). A small precipitate may form during the titration, but this will redissolve. The titration should be performed slowly with mechanical stirring. As the end-point is approached the permanganate should be added drop by drop, and time allowed for the completion of the reaction. The end-point is taken as the point of greatest change in potential for equal additions of permanganate. Should too much permanganate be added, the end-point may be approached from the other side by adding a standard solution of ferrocyanide. The presence of ferricyanides does not interfere with the titration, neither do amounts of chloride up to 1 gram of sodium chloride. Any salts which under the conditions of experiment produce a precipitate with either ferrocyanide or ferricyanide seriously interfere with the method.

J. F. S.

**Use of Silicotungstic Acid in the Estimation of Alkaloids.**

ERWIN TAIGNER (*Zeitsch. anal. Chem.*, 1919, **58**, 346—352).—Silicotungstic acid solution may be used for the quantitative precipitation of atropine, strychnine, and cocaine from their hydrochloric acid solutions; the precipitates formed are collected, after the addition of sodium chloride, washed with 1% hydrochloric acid, dried at 40°, and weighed. The precipitates have the general formula  $12\text{WO}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O} \cdot 4\text{-alkaloid}$ .

W. P. S.

**Colour Reactions of Emetine.** ABEL LAHILLE (*Arch. méd. exp.*, **27**, 296; *Zentr. Biochem. Biophys.*, 1919, **20**, 398).—Emetine hydrochloride develops a yellow coloration with calcium chloride and with concentrated nitric acid. When a small crystal of ammonium molybdate is added to a solution of the hydrochloride in concentrated sulphuric acid a green zone, which subsequently turns blue, is formed round the crystal; the colour disappears on dilution.

with water and reappears on heating. A green coloration is produced when a dichromate is used instead of ammonium molybdate.

CHEMICAL ABSTRACTS.

**The Arsenotungstic Reagent in the Method of Bertrand and Javillier for the Estimation of Nicotine.** LUIS GUGLIAMELLI and ULAUS HORDH (*Anal. Soc. Quim. Argentina*, 1919, 7, 121—123).—The preparation of silicotungstic acid for the estimation of nicotine by the method of Bertrand and Javellier (A., 1909, ii, 450) presents difficulties. The authors recommend the use of arsenotungstic acid (Guglielmelli, A., 1916, ii, 584, 587) as a precipitant. The procedure is otherwise unaltered. W. S. M.

**Ehrlich's Reaction with *p*-Dimethylaminobenzaldehyde and Urorosein.** E. SALKOWSKI (*Biochem. Zeitsch.*, 1919, 97, 123—129).—The reaction of *p*-dimethylaminobenzaldehyde with indole, indoleacetic, indolepropionic and indoleaminopropionic acids is described and discussed. Herter's theory concerning the origin of uroresin in urine is also discussed. S. S. Z.

**Estimation of Tyrosine by means of Millon's Reaction.** MORIZ WEISS (*Biochem. Zeitsch.*, 1919, 97, 170—176).—A 1:50,000 solution of tyrosine to which Millon's reagent is added is used as a standard. The solution to be examined is then diluted until it gives with Millon's reagent a coloration equal to that of the standard. The method can be employed for the estimation of tyrosine in the products of hydrolysis of proteins. S. S. Z.

**New Method of Estimating Albumin in Urine.** DOMENICO GANASSINI and PIETRO FABERI (*Boll. Chim. Farm.*, 1919, 58, 313—319).—A method of estimating albumin in urine is based on the fact that the sulphur of the cystinic group in the protein molecule is readily detached by the action of hot alkali hydroxide, and in presence of lead plumbite yields lead sulphide. On then titrating the liquid with iodine solution, the metaproteins are first oxidised and iodised, and the lead sulphide is then converted into lead sulphate. In applying the method, from 20 to 100 c.c. of urine (according to the amount of albumin indicated by a preliminary test) are mixed with 5% of sodium dihydrogen phosphate (to prevent precipitation of phosphates of alkaline earth metals), and the liquid heated and stirred for a few seconds until the albumin has coagulated. The precipitate is separated, washed, and dissolved in 10 to 30 c.c. of 10% potassium hydroxide solution, from 3.3 to 10 c.c. of 5% normal lead acetate solution added, and the beaker immersed for five minutes in boiling water. The liquid is then cooled to 21° and titrated with *N*/10-iodine solution, which is added at the rate of two drops per second, with continual stirring, until the liquid becomes colourless. The number of c.c. of iodine multiplied by 0.0330 gives the quantity of albumin in the amount of urine taken. Standard potassium ferri cyanide solution may be used instead of iodine solution for the titration, but the end-point of the reaction is not so sharp. C. A. M.

**Medical Analysis of Urine by the Combined Use of Tungstic Acid and Other Reagents.** HUGH CAMPBELL ROSS (Brit. Pat., 134710).—When to 2 c.c. of urine 0.2 c.c. of a reagent composed of a 12% aqueous solution of colloidal tungstic acid to which 10% of acetic or tartaric acid to neutralise any possible alkalinity of the urine, and 2.5% of sodium potassium tartrate have been added, the presence of albumin is indicated by the formation of a precipitate which does not dissolve on warming. If the acid is impure, an excess of urates also causes a precipitate, but it redissolves on boiling the solution. In the latter case, a diabetic condition is indicated, and the presence of reducing sugars may be tested for by adding copper sulphate and an alkali hydroxide, or preferably, for the sake of convenience, a tablet containing 0.02 gram of copper sulphate and 0.01 gram each of sodium carbonate and calcium hydroxide.

G. F. M.

**Volumetric Analysis of Ion-protein Compounds.** JACQUES LOEB (*Proc. Soc. Exp. Biol. Med.*, 1918, 16, 39).—Gelatin at  $p_H > 4.7$  combines only with cations and at  $p_H < 4.7$  only with anions, whilst at the isoelectric point ( $p_H = 4.7$ ) it combines with neither anion nor cation. Curves representing the influence of univalent anions or cations on the swelling, osmotic pressure, and viscosity of gelatin are always approximately parallel with the curves representing the amount of anion or cation found in chemical combination with the gelatin.

CHEMICAL ABSTRACTS.

**Estimation of Pepsin.** JOHN H. NORTHPROP (*J. Gen. Physiol.*, 1919, 2, 113—120).—See this vol., i, 193.

**Influence of Acetic Acid on the Benzidine Reaction.** EMMO SCHLESINGER and JULIUS GATTNER (*Berl. Klin. Woch.*, 1919, 56, 706—707; from *Chem. Zentr.*, 1919, iv, 526).—The discordant views of different authors on the value of the benzidine reaction in the detection of blood are due to the previously unnoticed fact that the sensitiveness of the reaction is a function of the concentration of the benzidine in the acetic acid. The authors find that a blue substance is the actual product of the benzidine reaction; this is precipitated if the proportion of acetic acid to benzidine is low, and is thus removed from further action and remains stable for a long period. In the presence of an excess of acetic acid, however, it dissolves, with the formation of a very unstable, green solution. Diagnostic conclusions cannot therefore be immediately based on the occurrence of one or other coloration, since the quantity of acetic acid used is a decisive factor. The blue colour invariably becomes green on addition of acetic acid.

H. W.

**Reduced Eosin as a Reagent.** LUCIANO P. J. PALET and AMANCIO FERNANDEZ (*Anal. Soc. Quim. Argentina*, 1918, 5, 119—120).—Traces of blood in dilute solution may be detected by means of the fluorescence produced with an alkaline solution of the leuco-derivative of eosin. The substitution of fluorescein for eosin is recommended.

W. S. M.

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In view of the fact that the malonic acid was carefully purified and melted at the correct temperature, it is almost impossible that this would account for more than a small fraction of the increased temperature-coefficient. Otherwise visible amounts of liquid should have been observed at 125°, whilst actually no trace was noticed. Nevertheless, the criticism must be borne in mind until further experiments are made.

The discussion of the bearing these results may have on the radiation hypothesis may be left until the study of the infra-red properties is completed.

In conclusion, I have pleasure in thanking Mr. H. B. Hartley and Mr. D. H. Nagel for much help and advice.

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BALLIOL AND TRINITY COLLEGES,  
OXFORD.

[Received, December 18th, 1919.]

## XXI.—*Some Observations on the Action of Coal upon a Photographic Plate.*

By ERIC SINKINSON.

THIS paper is the outcome of an attempt to discover what constituent of the coal substance is responsible for its well-known action on a photographic plate in the dark.

W. J. Russell (*Proc. Roy. Soc.*, 1908, [B], 80, 376) found (1) that coal and resin (among other substances), when placed on or near a sensitised plate in the dark for varying periods of time, reacted in such a way that, on developing the plate, an image was obtained, (2) that such action is dependent on the presence of air or oxygen, and (3) that it also requires direct contact between coal and the plate. The interposition of glass, mica, or metal between the two will prevent it.

Clark, Wheeler, and Platt (T., 1913, 103, 1713) employed the method to show that cellulose has no action on a photographic plate, and from this concluded that the portion soluble in pyridine contained the resinic constituent of the coal substance, because it acted intensely. By treating the part soluble in pyridine with chloroform, the extract obtained was found to produce an image on a plate, whilst the residue gave no image. They concluded, therefore,



that the chloroform extract contained the resinic, and the residues the cellulosic, portions of the coal substance. The results of the experiments recorded in this paper throw doubt on this conclusion. Stopes has also shown that, of what she has termed the three visible ingredients of a banded, bituminous coal, namely, durain, clarain, and vitrain (*Proc. Roy. Soc.*, 1919, [B], 90, 470), the last-named has the strongest action on a photographic plate.

#### EXPERIMENTAL.

As already stated, the action of coal on a photographic plate depends on the presence of oxygen. Thus, if a piece of coal is placed on a plate in a light-tight box and all the air displaced by nitrogen, no action will result, even after a period of twenty-four hours at 40°. Further, a small quantity of water vapour will prevent any action, even in the presence of air. Moreover, if the box is exhausted, no image can be obtained.

In order to decide whether the said effect of oxygen is caused by some actual oxidation of the coal substance or by some specific action on the plate, it was found that light will affect a plate enveloped in nitrogen apparently to the same extent as in air. Therefore it would appear that the presence of oxygen is essential to the action of coal, but not to that of light.

A series of experiments was also carried out on a Brodsworth "soft" coal in order to find whether the continued exposure of it in an atmosphere of oxygen at 40° would reduce its power of affecting a photographic plate. The samples were exposed to oxygen in both blue- and red-tinted bottles, and also to strong white light, in order to see whether the rate of absorption was altered. This was not so; even in bottles covered with "Berlin black" the rate of absorption of oxygen was approximately the same as in plain white bottles. The coal, when completely saturated with oxygen, was placed on a photographic plate side by side with an untreated sample. The latter undoubtedly gave the more intense image on development of the plate. This would indicate that the absorption of oxygen is part of the mechanism of the action of coal on a photographic plate.

Russell tentatively suggested that the production of hydrogen peroxide may be responsible for the change in the photographic plate, because the effect can be imitated by a suitable application of it to a plate.

So far, it has been impossible to find a test sufficiently delicate or decisive to confirm his suggestions. Daylight in the fiftieth of a second can bring about a result far greater than that of coal

acting for a period of twelve hours. The minute quantity of substance in the sensitive medium of the plate involved in the reaction renders the difficulty of detecting a cause obvious.

It seemed first of all necessary to inquire into the stability at high temperatures of the constituents of the coal that can react on a photographic plate in the dark, and the following describes how this information was obtained.

#### A.

A sample of Manvers Main coal (containing 5.7 per cent. of water) was ground and dried at  $105^{\circ}$  in the usual way, and 15 grams were introduced into a distillation tube closed at one end. The open end was closed by a stopper, through which was fixed a delivery tube connected with an aspirator filled with a mixture of glycerol and water; a manometer was inserted to indicate the slightly reduced pressure maintained throughout the carbonisation.

The distillation tube and connexions were exhausted, and heat was applied by a gas furnace, the temperature of which was measured by a platinum-rhodium-platinum thermo-couple. The first experiment was made at  $300^{\circ}$ , and this was considered complete when no more volatile matters were expelled, that is, when gas ceased to be evolved; this took about six hours.

Similar experiments were made at  $500^{\circ}$ ,  $700^{\circ}$ , and  $1000^{\circ}$ , the last being in a porcelain tube.

The residue was removed from the tubes in turn, ground to a coarse powder, and placed on a photographic plate in small heaps covered by inverted porcelain crucibles.

The plate\* was enclosed in a light-tight box and warmed in an incubator to  $40^{\circ}$  for twenty-four hours. It was then developed, with the result shown in the illustration.

(a) The dry sample gives the most intense image, the undried being slightly less in comparison.

\* An investigation was made to determine which type and speed of plate was most suitable for this work. In order to do this a large piece of coal was selected and smaller pieces of similar structure were broken from it and the surfaces rubbed flat. These were placed each on a different plate in a light-tight box which was warmed in an incubator for twenty-four hours. The plates used were Ilford "Monarch," Ordinary, Process, Chromatic, Panchromatic, Super Speed Ortho, and X-Ray. The Chromatic or Panchromatic gave no image. The Ordinary gave a poor image, Super Speed Ortho gave a fairly good one, but the best was obtained with an X-Ray plate. The only difference apparently between an X-Ray plate and the other type is that it has a slightly thicker film. Accordingly, the X-Ray type of plate was chosen for this work.

(b) The sample heated to 300° has much less effect; at 500° there is only very slight evidence of any action.

(c) At 700° and 1000° no action can be detected.

The black ring, so evident in the dried and undried original samples, is undoubtedly produced by the "vapour" pouring from the coal, as noted both by Russell and Wheeler under similar conditions.

### B.

It became necessary at this stage to study the action of coal heated to temperatures in the region of 500°; for the first series of experiments, which were repeated several times with different coals, establish the fact that the reactive principle is still present in the coal at this temperature.

Accordingly, the working temperatures chosen were 450°, 500°, and 550°. In order to make the investigation more comprehensive, coals of widely divergent origin were carbonised at these temperatures under exactly similar conditions, as follows:

(1) Two Spanish (coking and non-coking) bituminous coals of similar composition (kindly placed at my disposal by Prof. W. A. Bone), and

(2) Hamstead coal (Birmingham) and the ingredients of it, namely, durain, clarain, and vitrain, investigated by Stopes (*loc. cit.*)\*.

The two Spanish and the Hamstead coals, together with the ingredients of the last, were pulverised and dried. The six were then carbonised at the successive temperatures 450°, 500°, and 550°, as follows.

A weighed sample of each was placed in one of six separate hard glass tubes closed at one end, so as to form a retort, the open end being closed by a rubber stopper carrying a delivery tube. The six delivery tubes were connected to a common main, and so to a gasholder filled with glycerol and water. The whole of the gaseous products then entered the gasholder, which served to maintain an even reduction of pressure in all the distillation tubes.

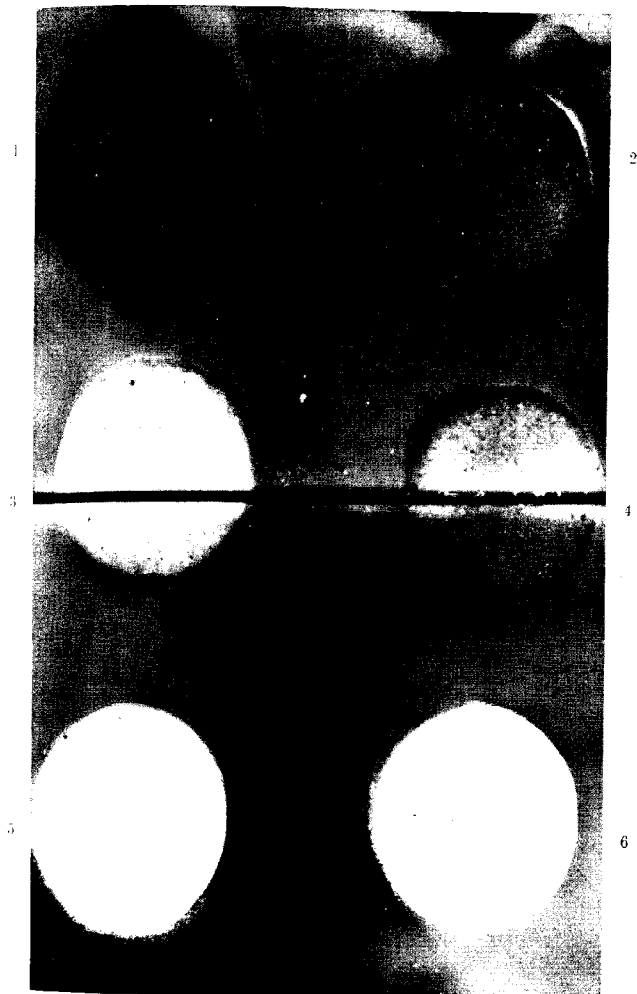
The tubes were heated together in an electric muffle furnace at the desired temperatures until all the volatile matter had been removed, for six hours as before. The temperature was measured by a calibrated platinum-rhodium-platinum thermo-couple.

\* "Durain" is the equivalent of "dull" hard coal or the "Matzkohle" of the Germans.

"Clarain" and "Vitrain" are the equivalent of "bright" or glaze coal, the "Glanzkohle" of the Germans.

"Vitrain" gives a conchoidal fracture, brilliant in appearance.

FIG. 1.



1. Dry coal before carbonising.  
3. Carbonised at 500°.  
5. Carbonised at 4000°.

2. Wet coal before carbonising.  
4. Carbonised at 300°.  
6. Carbonised at 700°.

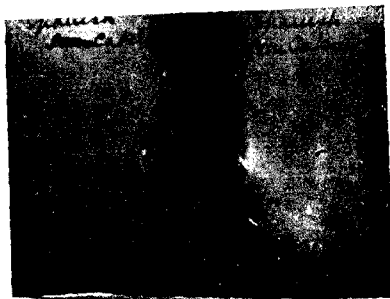
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Fig. 2.

1

2

450°



500°

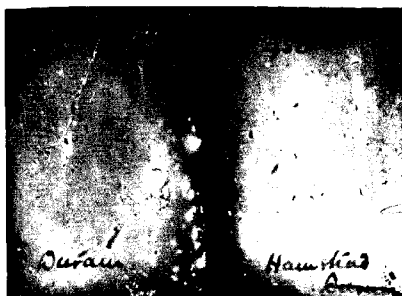


FIG. 3.

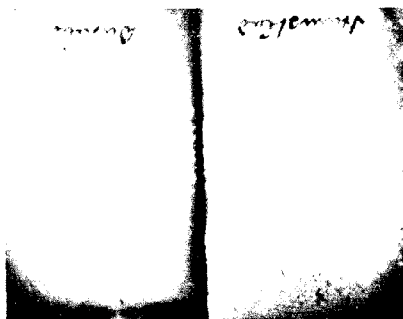
3

4

450°



500°



550°



3. Durain.

4. Hamstead.

FIG. 4.

5

6

450°



500°



550°



5. *Viteia*.

6. *Clarin*.

In this manner, the coals were carbonised under exactly comparable conditions at the three selected temperatures.

The residues were coarsely powdered and placed in turn on photographic plates, six heaps on each plate. The plates were contained in cardboard boxes, and these were placed in a specially constructed light-tight box, so that the carbonised products of the coals could be subjected to strictly comparable conditions.

The box was placed in an incubator, maintained at  $37^{\circ}$ , for three weeks, after which time the plates were removed and developed together at the same temperature. In order to give a positive effect on the prints, the plates were "printed" on to other plates, from which the illustrations shown were taken.

#### *Discussion of Results.*

The coals and separate ingredients carbonised at  $450^{\circ}$  give images on a photographic plate in the dark, but at  $500^{\circ}$  the effects are not so intense, although in some cases, such as Hamstead and durain, there is a decided diminution of effect.

For a carbonising temperature of  $550^{\circ}$  the effect is not perceptible, except perhaps in the case of the Hamstead, which is just perceptible. The critical point lies between  $500^{\circ}$  and  $550^{\circ}$ .

At  $450^{\circ}$  vitrain undoubtedly gives relatively the most intense image; at  $500^{\circ}$  this dies away rapidly.

Clarain is next in intensity, and also diminishes at  $500^{\circ}$ . Durain is less intense than either vitrain or clarain at a carbonising temperature of  $450^{\circ}$ , and dies away rapidly at  $500^{\circ}$ .

The order of these intensities bears out what Stopes found for these ingredients at the ordinary temperature.

The Hamstead coal carbonised at  $450^{\circ}$  gives the same order of intensity as durain, perhaps a little less marked, and this effect dies away rapidly at  $500^{\circ}$ , but is still faintly perceptible at  $550^{\circ}$ .

The Spanish coking and non-coking coal give similar degrees of intensity at  $450^{\circ}$ , but, unlike the others, the effect persists more strongly at  $500^{\circ}$ . They show, however, no trace of effect at  $550^{\circ}$ .

Russell's failure to obtain an image on a photographic plate from a coal which had been heated at  $200^{\circ}$  for twenty-four hours, a period far beyond that required to expel completely the volatile matters at that temperature, raises an interesting point in connexion with the destruction of the coking properties of coal by continued heating. De Marsilly in 1857 found that all coking coals lost their property of forming coke after being heated at  $300^{\circ}$  for some time. Anderson explains this by assuming the presence of a "resinoid" substance responsible for the coherence



of a coking coal. If, then, it be true that a resinic substance is responsible for the coking property of a coking coal, which can be destroyed by continued heating, also that the reactivity to a photographic plate can be traced to the same principle, the cause is explained.

In the present series of experiments, the coking coals, namely, the Spanish, carbonised at 500°, gave quite a good coke after heating for six hours, a time sufficiently long to expel all the volatile matters at that temperature.

Since resin has a similar effect to coal on a plate, and coal is known to contain resin, it might be considered reasonable to conclude that resin in coal is the activating agent towards the plate.

This conclusion was contradicted when, during the course of an unpublished research in conjunction with Prof. Bone, the author found that the pure resin, or, more precisely, the resin portion of resin, produces no effect on a photographic plate in the dark.

Clark, Wheeler, and Platt obtained an intense effect from the pyridine extract of a coal, and this is believed to contain, among other substances, the resinic constituents. It would seem, therefore, that in the pyridine extract is to be found the ingredient causing the action on a photographic plate, and the remaining constituents of this extract, other than the resin, should be responsible for this effect.

This question is now under investigation.

In conclusion, the author desires to record his best thanks to Prof. W. A. Bone for his interest in the work; to Drs. Wheeler and Stopes for the loan of the specimens of Hamstead coal; to Dr. Stopes, in addition, for the specimens of durain, clarain, and vitrain; and to Mr. Ernest Bury, M.Sc., for granting him certain facilities at the Skinningrove Iron Company's works for the prosecution of the work during July and August, 1919.

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XXII.—*The Sorption of Hydrogen by Palladium at Low Temperatures.*

By JAMES BRIERLEY FIRTH.

IN a previous communication (Holt, Edgar, and Firth, *Zeitsch. physikal. Chem.*, 1913, **82**, 513), a summary of the views held on the sorption of hydrogen by palladium is given. The view is also advanced that sorption takes place through an amorphous metallic phase, which acts as a carrier for the hydrogen to the crystalline metal. Further, the activity of the palladium is determined by the presence of the amorphous variety on the film. This amorphous variety is metastable, hence the decay in activity is due to the disappearance of this variety. It can be reproduced on the surface by heating to a red heat in a vacuum or in hydrogen, or by oxidising the surface and then reducing the oxide in hydrogen; the activity of the palladium can therefore usually be renewed by one of these methods.

Andrew and Holt (*Proc. Roy. Soc.*, 1913, [A], **89**, 170), from a consideration of the heating and cooling curves in hydrogen, find further evidence of two states of the metal. The rapid occlusion of this gas is attributed to the presence of the amorphous variety. In absence of the amorphous film, the palladium may be quite passive in the cold, or at any rate the sorption may be exceedingly slow. At temperatures above 100°, no matter whether the palladium be originally passive or active, a rapid occlusion of a small amount of hydrogen invariably takes place. At temperatures above 150°, all forms of palladium have equal affinity for the gas.

Halla (*Zeitsch. physikal. Chem.*, 1914, **86**, 496), in a criticism of the above two communications, expresses the view that the palladium, characterised by Graham as inactive, is not really inactive, but apparently so owing to a film of occluded oxygen on the surface.

Holt (*Proc. Roy. Soc.*, 1914, [A], **90**, 226), from a study of the rate of solution of hydrogen by palladium, draws the following conclusion: "The rate of solution of hydrogen by palladium is not a simple function of the concentration of the gas in the metal. The rate curves consist of two portions (except in the case of palladium black), which have been interpreted as referring to solution in two different forms of the metal. The smooth rate curve for palladium black is taken to mean complete absence of one of these forms."

Paal and Amberger (*Ber.*, 1905, **38**, 1394) determined the

occlusion of hydrogen by palladium black at  $-10^{\circ}$  by heating in hydrogen at  $110^{\circ}$  and cooling to  $-10^{\circ}$ , and found the amount of hydrogen considerably increased.

Gutbier, Gebhardt, and Ottenstein (*Ber.*, 1913, **46**, 1453), by the same method as Paal and Amberger, determined the occlusion down to  $-50^{\circ}$ , and found occlusion considerably increased with diminution of temperature.

Sieverts (*Zeitsch. physikal. Chem.*, 1914, **88**, 105), in two communications, shows that from  $100^{\circ}$  to  $1500^{\circ}$  occlusion diminishes with rise of temperature. Palladium black at  $137^{\circ}$  occludes larger volumes than foil at the same temperature. At higher temperatures, amorphous and crystalline palladium occlude hydrogen by solution merely; at lower temperatures, amorphous palladium takes up further quantities by adsorption.

S. Schmidt (*Ann. Physik*, 1904, [iv], **13**, 747) finds that at temperatures between  $140^{\circ}$  and  $300^{\circ}$  the volume of hydrogen occluded increases with fall of temperature; below  $140^{\circ}$ , the results were not concordant.

Partington (*Trans. Faraday Soc.*, 1919, **14**, 259) calculates the heat of dissociation of hydrogen from the dissociation pressures of "palladium hydride" given by Troost and Hautefeuille (*Compt. rend.*, 1874, **78**, 686), and obtains the value 4568 gram-calories, which is in close agreement with the experimental value, 4672, obtained by Mond, Ramsay, and Shields (*Trans. Roy. Soc.*, 1898, [A], **191**, 105).

The object of the experiments described in the present communication was to study the activity of palladium at low temperatures, in particular at the temperature of liquid air and at  $0^{\circ}$ , and, so far as possible, to determine the equilibrium pressures under these conditions. Previous investigators have apparently had as their object the maximum volumes which can be occluded by palladium at low temperatures, and have started occlusion at some higher temperature and cooled the palladium to the required temperature (compare Paal and Amberger). In the present work, the maximum occlusion attainable was not given any special consideration. It is the opinion of the author that the existence of at least two allotropic modifications of palladium has already been proved, namely,  $\alpha$ -, or amorphous, palladium, and  $\beta$ -, or crystalline, palladium. The  $\alpha$ -form is highly active, and is responsible for rapid occlusion at temperatures up to about  $150^{\circ}$ ; it is further capable of acting as a carrier to the  $\beta$ -variety, which may be completely passive or moderately active, according to conditions of temperature.

The term "adsorption" is used to indicate rapid occlusion of

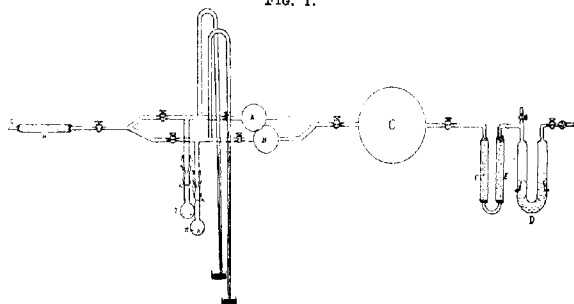
hydrogen, that is, where diffusion is not a determinable factor. "Absorption" denotes the slower process, in which the rate of diffusion or solution is a determinable factor. "Sorption" is used as a collective term, and includes adsorption and absorption (compare McBain, *Phil. Mag.*, 1909, [vi], **18**, 916).

#### EXPERIMENTAL.

The apparatus used is indicated in Fig. 1. Bulbs I and II are of quartz, and contain the palladium, each bulb being connected to a separate manometer. *A* and *B* are reservoir bulbs of about 250 c.c. capacity. *C* is a large bulb of about 1 litre capacity used as a reservoir for hydrogen.

The hydrogen was prepared by the electrolysis of barium hydro-

FIG. 1.



oxide in U-tube *D*, and dried by passing through tubes *E* and *F* containing phosphoric oxide.

The apparatus can be exhausted through tube *G*, which is connected with a Toepler pump, *H* being a drying tube containing phosphoric oxide. Bulbs I and II were immersed in cooling baths to *h* and *h'* respectively.

The palladium foil used in these experiments was from the same sample as that employed in the previous research (Holt, Edgar, and Firth, *Zeitsch. physikal. Chem.*, 1913, **82**, 513).

Bulb I contained 1.0075 grams of palladium foil, and bulb II 1.0100 grams.

(a) The palladium, as received, was exposed in bulb I to hydrogen at the ordinary temperature ( $16.8^{\circ}$ ) and atmospheric pressure (758 mm.). Bulb II was immersed in liquid air, and then hydrogen admitted to atmospheric pressure.

The manometer remained at zero for more than four hours, no hydrogen being sorbed in either case, that is, the palladium was inactive.

(b) The palladium in bulbs I and II was heated to a red heat in a vacuum for about five minutes, bulb II was then immersed in liquid air, and bulb I kept at the ordinary temperature ( $16.4^{\circ}$ ), both samples being exposed to hydrogen under atmospheric pressure (757 mm.). After four hours, the liquid air was removed, and both samples were left in contact with hydrogen overnight at the ordinary temperature. Next morning, the amount of hydrogen sorbed by 1 volume of palladium (volumes of hydrogen corrected to N.T.P.) was as follows:

Bulb I, 10 vols.

Bulb II, 0 vol.

(c) Experiment (b) was repeated, with the following result:

Bulb I, 12 vols.

Bulb II, 3 vols. (approx.).

(d) The palladium in bulbs I and II was heated to a red heat in a vacuum for one hour, and then exposed to hydrogen exactly as in (b). Result:

Bulb I, 14 vols.

Bulb II, 3.5 vols.

From the above results, it appears that heating in a vacuum has failed to activate the palladium to any great degree, and, further, the sample immersed in liquid air always gave a lower result.

(e) The palladium from each bulb was then transferred to a crucible and heated in air for two hours in order to coat it with a thin film of oxide, the palladium then being returned to the bulbs. The bulbs were exhausted, bulb II was immersed in liquid air and then exposed to hydrogen at atmospheric pressure, and bulb I exposed to hydrogen at the ordinary temperature ( $15.8^{\circ}$ ) and atmospheric pressure (758 mm.). Result:

BULB I.		BULB II.	
Hydrogen rapidly sorbed:		No hydrogen sorbed while in liquid air	
10 mins. ...	240 vols.	(6 hours). After 6 hours, liquid-air bath	
11 mins. ...	432 "	removed, no sorption took place for 25	
Next morning ...	684 "	minutes, then sorption began, slowly at	
		first, with increasing rapidity.	
		30 mins. after removal of liquid air	10 vols.
		35 " " "	37 "
		40 " " "	108 "
		45 " " "	227 "
		Next morning " ... "	525 "

(f) The palladium in bulb II was oxidised by heating in air for two hours and the bulb exhausted. About 1 c.c. of hydrogen was admitted to reduce the oxide, and the bulb again exhausted. It was then immersed in liquid air and hydrogen admitted to atmo-

spheric pressure. No sorption took place during a period of six hours, when the liquid air was removed and the palladium allowed to attain the ordinary temperature. After thirty-two minutes, sorption began, and finally 742 volumes were sorbed.

(g) The palladium in bulb I was oxidised by heating in air for two hours, and then exposed to hydrogen under atmospheric pressure. Hydrogen was taken up immediately, and, after 377 volumes had been sorbed, the bulb was immersed in liquid air, with the result that sorption ceased; after three hours, the liquid-air bath was removed and the palladium allowed to attain the ordinary temperature. After ten minutes, hydrogen was rapidly sorbed, and finally 798 volumes were taken up.

After expelling the hydrogen from the palladium in each case at a dull red heat, and when the palladium had again reached the ordinary temperature, the samples were immediately exposed to hydrogen, but no sorption took place, even after a period of two days, therefore the palladium had become inactive.

From the above experiments, it would appear (a) that "active" palladium is "inactive" at liquid-air temperature; (b) that the immersion in liquid air tends to retard the activity at the ordinary temperature, and to some extent to lower the sorption value.

The film of oxide on the palladium did not appear to have been removed while in the liquid-air bath in experiment (e).

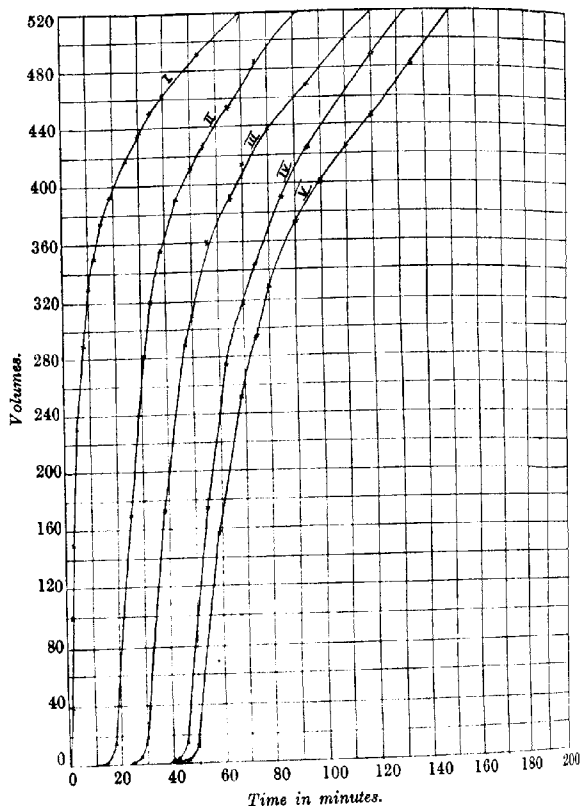
In order to determine more fully the influence of liquid air on the activity of palladium, the following experiments were made.

Before each experiment, the palladium was activated by heating it in air for two hours, thus becoming coated with a thin film of oxide. The only difference between each experiment was in the length of time of cooling at liquid-air temperature. After the removal of the liquid air, the bulb was dried externally, and, after a lapse of five minutes, exposed to hydrogen at the ordinary temperature and atmospheric pressure. The rates of sorption were then observed, and the results obtained are shown graphically in Fig. 2. The first curve is the normal curve, the palladium having been exposed to hydrogen at the ordinary temperature ( $16.5^{\circ}$ ) without any previous cooling. Curves II, III, IV, and V represent the results after previous cooling in liquid air for one, three, six, and nine hours respectively. On comparing the results, it appears that there is a definite "lag" in the activity of the palladium after cooling in liquid air, and, further, the longer the periods of cooling the longer is the "lag." When the sorption does commence, it is very slow at first, but soon becomes normal.

From the foregoing experiments, it would appear that not only is the palladium, which is active at the ordinary temperature,

inactive at liquid-air temperature, but on returning to the ordinary temperature it is temporarily passive to hydrogen, the period of passivity depending on the duration of cooling. It is clear that this passive condition of palladium is different from the variety

FIG. 2.

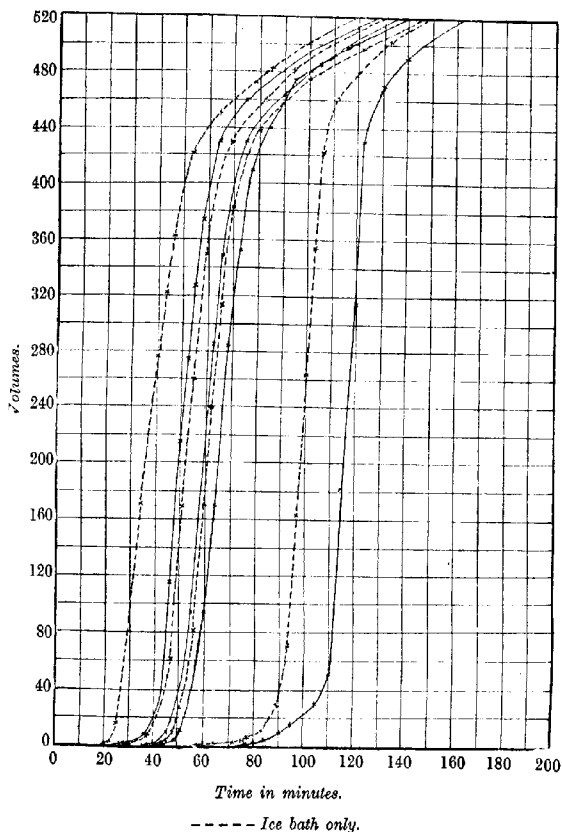


which is "dead," irrespective of the time of contact with hydrogen, since it returns to normal activity.

In order to delay the transformation from the "passive" to the "active" condition, another series of experiments was made which differs from the series just described only in the temperature at which the palladium was exposed to hydrogen. In this series, the

palladium was placed in a bath of melting ice immediately on removal of the liquid-air bath. These experiments were carried out in bulb I, and simultaneously a second series in bulb II was carried out in which the palladium was cooled in an ice-bath for

FIG. 3.



the same period as bulb I was cooled in liquid air before exposing to hydrogen at  $0^{\circ}$ . The results obtained in both cases are shown graphically in Fig. 3. Commencing from the left of the diagram, the continuous curves represent the results after cooling with liquid



air for one, three, six, and nine hours, respectively, prior to exposure to hydrogen at  $0^{\circ}$ .

The broken curves represent the results after cooling at  $0^{\circ}$  for one, three, six, and nine hours, respectively, prior to exposure to hydrogen at  $0^{\circ}$ .

From these results, it would appear that not only does the ice-bath increase the period of passivity of the palladium after cooling in liquid air, but also the palladium becomes passive after cooling at  $0^{\circ}$ . After a time, however, sorption begins, even at  $0^{\circ}$ ; the rate is very slow at first, but finally reaches a normal one.

In all cases, the period of "lag" increases with time of previous cooling.

Further experiments were made in which additional precautions were taken and any disturbing factors eliminated so far as possible.

It was observed that several of the pieces of foil were very much pitted by repeated use, so fresh pieces of foil, each about 0.25 sq. cm., with smooth surfaces were selected.

1.0105 Grams of foil were oxidised by heating in air for four hours in order to obtain a uniform film, and then carefully introduced into bulb I, and again heated in air to oxidise any portion which had been accidentally rubbed while being transferred to the quartz bulb. The bulb was exhausted and cooled in a double ice-bath for twenty-four hours, after which period hydrogen was carefully admitted. Care was taken to eliminate any vibration by avoiding unnecessary movement in the vicinity of the apparatus and by not disturbing the apparatus during the replenishing of the ice-baths.

By taking all conceivable care, a permanent period of inactivity seemed to be obtained. The palladium remained inactive for forty-eight hours, after which the activity under ordinary conditions was tested by the removal of the ice-bath. The palladium remained inactive for a further period of 145 minutes, after which sorption began, the rate being slow at first. The results were as follows:

145 mins.	...	...	0.0 vol.
175 "	...	...	10.3 vols.
190 "	...	...	98.6 "
195 "	...	...	187.8 "
Final	...	...	778.5 vols. (excluding initial adsorption)

Several attempts were made to repeat this experiment, and four consecutive experiments gave the following periods of passivity: (a) 5 hours; (b) 3 hours 37 minutes; (c) 48 hours; (d) 7 hours 11 minutes. In experiment (c), the passivity was considered permanent, and the ice-bath was removed at the end of two days. The final volumes sorbed in the above cases were: (a) 810 vols.;

(b) 805 vols.; (c) 803 vols.; (d) 792 vols.\* Why sorption commenced in experiments (a), (b), and (d) is not quite clear from the present information, but possibly some local disturbance occurred.

In all experiments at  $0^{\circ}$ , the oxide appeared to be reduced immediately on admission of hydrogen. In order to test this point, a further series of experiments was performed in which the oxide was first reduced by admitting 1 c.c. of hydrogen before cooling to  $0^{\circ}$ , exhausting as completely as possible, and cooling at  $0^{\circ}$  for twelve hours before admitting hydrogen. The periods of passivity in five experiments were: (a) 7 hours 10 minutes; (b) 45 minutes; (c) 26 hours 19 minutes; (d) 15 hours 42 minutes; (e) 11 hours 17 minutes.

The volumes sorbed were: (a) 812 vols.; (b) 819 vols.; (c) 807 vols.; (d) 798 vols.; (e) 817 vols.\*

The palladium in bulb I was heated in air for two days; the oxide film was reduced by admitting 1 c.c. of hydrogen, and then allowed to remain for two days at the ordinary temperature in a vacuum. Hydrogen was then admitted at the ordinary temperature and atmospheric pressure (757 mm.). The gas was slowly sorbed, and, after twenty-four hours, only 227 volumes of gas had been occluded. Hence the  $\alpha$ -variety had been largely transformed into the  $\beta$ -variety.

In order to test further the reduction of palladium oxide at  $0^{\circ}$ , 0.5 gram of palladium oxide was cooled in bulb I for one hour, and then exposed to hydrogen. The oxide was instantly reduced.

In the experiments previously described, the hydrogen was admitted until atmospheric pressure was reached, an operation which only took a few seconds, but rapid adsorption (if any) would take place during the admission of the hydrogen and would not be recorded on the manometer. In order to determine the extent of such adsorption, the following experiments were made.

(a) 1.0150 Grams of inactive palladium were exposed to hydrogen at  $16.7^{\circ}$  and atmospheric pressure (758 mm.). The bulb was immersed in liquid air, when the manometer rose rapidly, and then remained steady. Hydrogen was next admitted until the pressure was atmospheric. The bulb was then opened to the pump and the liquid-air bath removed, the hydrogen being pumped off and measured. After correcting for adsorption by the wall of the quartz bulb (from a blank experiment), it was found that 143.9 volumes of hydrogen had been adsorbed.

(b) The palladium was rendered active by oxidising the film in air. It was then cooled to liquid-air temperature and exposed to

\*Excluding the initial adsorption which took place immediately on admitting hydrogen.

hydrogen under atmospheric pressure. The volume of gas adsorbed was measured as before. On attaining the ordinary temperature, some of the gas passed into the interior of the metal, and the last traces of hydrogen were removed by heating to a dull red heat. The volume of the gas corresponded with an adsorption of 317 volumes.

(c) Similar experiments at  $0^{\circ}$  gave adsorptions of 17.5 vols. and 45 vols. respectively. In the case of active palladium, measurement was made after fifteen minutes and before any apparent diffusion into the interior of the metal had taken place.

(d) Palladium activated by oxidising in air was saturated with hydrogen at the ordinary temperature and atmospheric pressure, and approximately 815 vols. were taken up. The palladium was then cooled in liquid air, the hydrogen being maintained under atmospheric pressure. The total gas was measured as before, the last portion of hydrogen being evolved by heating to a dull red heat. Hydrogen corresponding with a sorption of 1156 vols. was collected, being an addition of 341 vols., due to cooling.

(e) A similar experiment at  $0^{\circ}$  gave an increase of 74.5 vols. over that sorbed at the ordinary temperature.

(f) Active palladium was saturated with hydrogen at liquid-air temperature, as described in experiment (d), and as much as possible was removed while at liquid-air temperature. After pumping off the gas for six hours, 415 vols. of gas were removed, and the manometer registered a vacuum. After remaining for one hour, no change in pressure was observed, and it was not possible to pump off measurable quantities of gas at this temperature within a reasonable time. On removing the liquid-air bath and heating to redness, 727 vols. of gas were evolved.

(g) Active palladium was cooled in a freezing mixture at  $-11^{\circ}$  in a vacuum for thirty minutes, and then exposed to hydrogen under atmospheric pressure. No absorption took place after twelve hours' contact, and 117 vols. of hydrogen were adsorbed.

(h) Active palladium saturated with hydrogen at  $15.7^{\circ}$ , then cooled in a freezing mixture to  $-11^{\circ}$ , gave a total sorption of 987 vols.

#### *Determination of Equilibrium Pressures at $0^{\circ}$ .*

The palladium was oxidised by heating in air for thirty minutes, the bulb immersed in an ice-bath, and, after ten minutes, exposed to successive quantities of hydrogen, equilibrium being attained after each addition.

On the first addition there was a lag of twenty-three minutes,

on the second addition a lag of three minutes, but on each subsequent addition sorption began immediately.

The results are given in table I, and are shown graphically by curve *AB* in Fig. 4.

TABLE I.

C.c. of gas occluded by 1 vol. of metal .....	55.8	116.2	782.5	260.6	336.8
Equilibrium pressure in mm. ...	6.5	8.4	10.5	12.75	14.8
$\sqrt{P_{AB}}$ .....	—	2.92	3.24	3.57	3.87
$P_{AC}^*$ .....	—	1.9	3.0	3.2	3.7
$P_{AB}^2/V$ .....	—	0.6082	0.6057	0.6243	0.6501

C.c. of gas occluded by 1 vol. of metal .....	405.4	460.4	544.3	571.6	613.5
Equilibrium pressure in mm. ...	26.5	36.3	72.8	87.5	105.9
$\sqrt{P_{AB}}$ .....	5.15	6.02	8.53	9.35	—
$P_{AC}^*$ .....	4.6	5.6	8.4	9.6	—
$P_{AB}^2/V$ .....	1.734	2.828	9.7	13.4	—

\* From graph *AC* Fig. 4.

The hydrogen was then removed in successive stages and the "equilibrium" pressure determined after each removal. The results are given in table II and shown graphically by curve *AC* in Fig. 4.

TABLE II.

C.c. of gas occluded by 1 vol. of metal	613.5	597.1	576.6	525.2	452.1	376.5	297.9	212.1	163.1	94.8
Equilibrium pressure in mm. ....	105.9	18.2	10.2	7.6	5.8	4.4	3.5	3.1	2.5	1.5

It will be observed that for the same concentration of hydrogen there are two "equilibrium" pressures, and a similar result was obtained by Holt, Edgar, and Firth (*Zeitsch. physikal. Chem.*, 1913, **82**, 513). In this case, the difference in the two cases is not so marked. The curve *AB* at 100° showed no horizontal portion, and was not in any way similar to *AC*, whereas at 0° the results give similar curves.

The curve *AB* may be taken to represent the equilibrium pressures of "adsorbed" hydrogen, and *AC* (lower portion) that of the "absorbed" hydrogen.

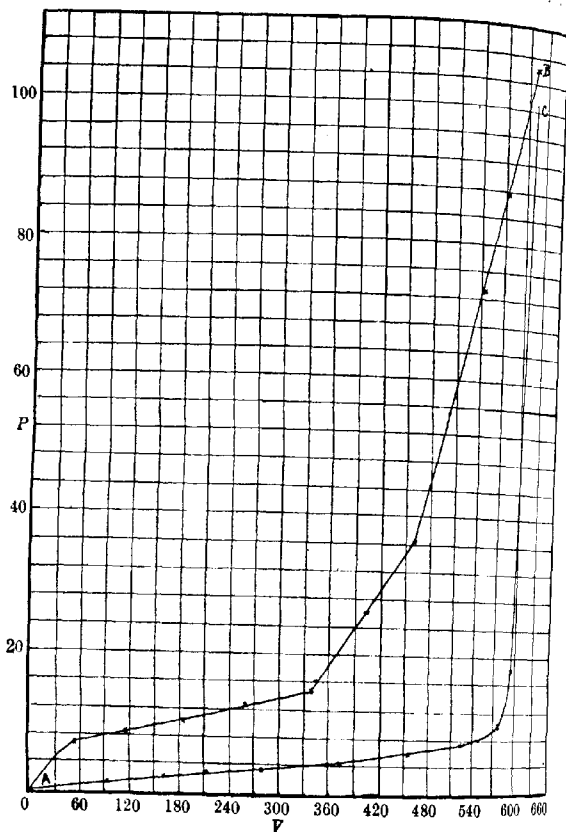
The relationship between the two sets of results may be approximately represented thus:

$$V\sqrt{P_{AB}} = VF_{AC} \quad \text{or} \quad \sqrt{P_{AB}} = \sqrt{F_{AC}}.$$

In table I values for  $P_{AB}^2/V$  are given, and the results show that

below 400 vols. the value approaches a constant; similarly,  $P_{ac}^4/V$  would approach the same constant. These results would indicate a difference in molecular complexity between the hydrogen in the surface layer and that in the interior of the metal.

FIG. 4.



#### Conclusions.

The inactivity of the palladium used in the first three experiments cannot be reasonably attributed to the presence of a film of oxygen, as suggested by Halla, since in the second and third experi-

ments a small amount of hydrogen was occluded and expelled by heat, which would remove the last traces of oxygen.

Sieverts and others have shown that at high temperatures the occlusion of hydrogen is one of simple solution, or "absorption," whilst the experiments herein described show that at low temperatures "adsorption" only takes place. The limiting temperature for diffusion into the interior is probably about  $0^{\circ}$ . Where the palladium has been previously saturated with hydrogen and cooled to a temperature below  $0^{\circ}$ , the increase in volume is due to adsorption.

The conclusions may be briefly stated thus:

- (a) Below  $0^{\circ}$ , adsorption only.
- (b)  $0-150^{\circ}$ , adsorption followed by absorption.
- (c) Above  $150^{\circ}$ , absorption only.

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### XXIII.—*The Interaction of Chlorine and Marsh Gas under the Influence of Light. The Conversion of Methyl Chloride to Methyl Alcohol and Methyl Acetate.*

By JOHN REGINALD HARVEY WHISTON.

THE photochemical interaction of chlorine and methane has been the subject of several investigations. Frankland (*Quart. Journ. Chem. Soc.*, 1850, **3**, 338), who first studied the reaction, believed that the principal product was methyl chloride when equal volumes of the two gases were taken, and principally methylene dichloride when the volume of the chlorine was twice that of the methane. Berthelot (*Ann. Chim. Phys.*, 1858, [iii], **52**, 97) stated that one-third of the residue obtained after the removal of hydrogen chloride from the products of interaction of equal volumes of methane and chlorine in diffused daylight was methyl chloride. J. Walter (D.R.-P. 222919) has patented a method of chlorinating methane under the action of light, whilst C. W. Bedford (*J. Ind. Eng. Chem.*, 1916, **10**, 1090) effects the chlorination of natural gas in a chamber containing ice with light from the white flame arc. The latter investigator states that the principal liquid products of the reaction are methylene dichloride and chloroform, up to 40 per

cent. of methyl chloride being present in the gases removed from the chamber after the reaction has been proceeding for a few minutes.

The present work was originally undertaken in order to determine whether it was possible to convert a sufficiently large proportion of the chlorine into methyl chloride to employ the reaction as an economic method of synthesising methyl alcohol on the large scale, as it has been shown by D. L. Chapman that methyl chloride can be almost quantitatively hydrolysed to methyl alcohol under the proper conditions. It was found, however, that not more than 25 per cent. of the chlorine forms methyl chloride in a mixture of  $2\frac{3}{4}$  volumes of methane to 1 volume of chlorine, and only 10–13 per cent. in a mixture of equal volumes.

#### EXPERIMENTAL.

In the first series of experiments, natural gas from a blower in South Wales, containing a high percentage of methane, and commercial liquid chlorine were used, no attempt being made to purify them, except that they were dried, the marsh gas by passage through a long tube of calcium chloride, the chlorine by concentrated sulphuric acid. Preliminary experiments made with mixtures of marsh gas and chlorine in the ratio 2:1 showed that there was no combination in the dark, a slow combination under the influence of light from an ordinary 60-watt metallic filament lamp placed 30 cm. from the reaction vessel, and a much more rapid combination if an arc light was used. It was incidentally observed that if the gases contained a very small amount of nitrosyl chloride, practically no action took place, even in the strongest light.

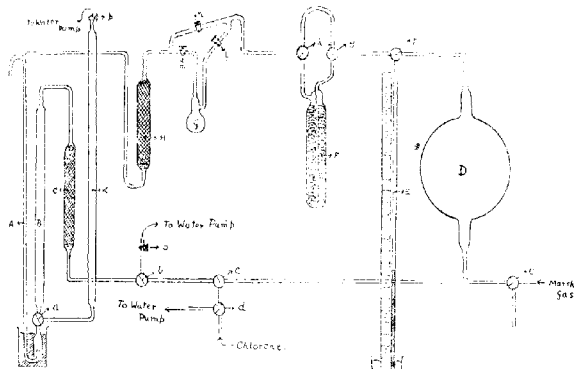
The quantitative estimation of the methyl chloride produced in the photochemical interaction of measured volumes of chlorine and marsh gas was effected with the aid of the apparatus depicted on p. 185.

*Method of Separation of the Products of the Reaction.*—The hydrogen chloride formed was easily removed by circulation through the tubes of soda-lime. The separation of the methyl chloride from the higher chlorinated products was more difficult, but advantage was taken of the large difference between the boiling points of methyl chloride and these other products, the various boiling points being:

Methyl chloride .....	−24.1°
Methylene dichloride .....	41.6°
Chloroform .....	61.2°
Carbon tetrachloride.....	76.7°

The method adopted, therefore, was to condense the methylene dichloride, chloroform, and carbon tetrachloride in the small condensing apparatus by a freezing mixture of carbon dioxide and ether and then to raise the temperature of the condensing apparatus to  $0^{\circ}$ , when any condensed methyl chloride evaporates, and this, together with the uncondensed methyl chloride, is then condensed in the charcoal tube, the latter being kept at  $0^{\circ}$ . A small amount of marsh gas also condenses in the charcoal, but by a test experiment made with a mixture of marsh gas and methyl chloride (prepared by the method due to Groves, *Journ. Chem. Soc.*, 1874, 27, 641), it was shown that, provided the charcoal was kept at  $0^{\circ}$ , the

FIG 1.



A—Sprengel pump.

B—Tube in which the gases pumped out by the pump could be collected.

C—Tube packed with soda-lime to absorb hydrogen chloride formed in the reaction.

D—The reaction vessel of about 1750 c.c. capacity.

E—Manometer.

F—Tube packed with wood charcoal.

G—A small condensing apparatus capable of being inserted in a thermos flask.

H—Tube packed with calcium chloride and soda-lime.

K—Tube communicating through a three-way tap with the collector B.

The three-way taps in the apparatus are denoted by *a, b, c, d, e, f, g*, and *h*; and the two-way taps by *l, m, n, o*, and *p*.

The various portions of the apparatus were divided into four volumes:

$V_1$ —From two-way tap *o* through *b, c, D* to *f*.

$V_2$ —From three-way tap *b* through *C* to a fixed mark on the collector B.

$V_3$ —From three-way tap *f* through *g, h* (omitting the charcoal tube F) to two-way taps *l* and *n* on the condensing apparatus G.

$V_4$ —The volume of the condensing apparatus between taps *l* and *m*.



condensed marsh gas could be pumped off without removing any appreciable amount of the methyl chloride. The latter could be pumped off if the charcoal tube was heated to  $300^{\circ}$  by immersion in a tube of concentrated sulphuric acid. No attempt was made to separate the higher chlorinated products of the reaction from each other.

*Experimental Details.*—The method of conducting an experiment was as follows:

(1) The entire apparatus was first exhausted by the Sprengel pump.

(2) Marsh gas, dried by passing slowly through a tube packed with calcium chloride, was then admitted to the volume,  $V$ , through tap  $e$  until the required amount as shown by the manometer had been admitted.

(3) The three-way tap  $b$  was then opened to allow the marsh gas to fill the volume,  $V_1$  also.

(4) Chlorine, dried by concentrated sulphuric acid, was then admitted through tap  $c$  into the volume,  $V$ , until the required amount had been admitted.

*Note.*—The admission of chlorine was always carried out in red light.

(5) The chlorine was then swept out of the capillary tubes into the reaction globe,  $D$ , by increasing the pressure on the marsh gas in the volume,  $V_1$ , by means of mercury admitted into the collector from the side-tube  $K$ , and then momentarily opening tap  $b$ .

(6) The mixture was allowed to remain overnight to ensure that the chlorine had completely diffused through the marsh gas. From daybreak (about 5 a.m.) until 9 a.m. the mixture was exposed to daylight admitted through the windows of the laboratory, and then, although the green colour of the chlorine had completely disappeared, it was exposed for about one hour to the arc light to make sure that combination was complete. That this was so was further shown by the fact that the mercury in the apparatus was not attacked during the remainder of the experiment.

(7) The condensing apparatus was then immersed in a freezing mixture of carbon dioxide and ether, and the gaseous mixture circulated through the whole of the apparatus (except the charcoal tube) by means of the Sprengel pump. When the manometer indicated that no further condensation would occur, circulation was stopped.

(8) Iced water was then substituted for the carbon dioxide and ether, the charcoal tube also surrounded by iced water, tap  $m$  closed, tap  $n$  opened, and circulation recommenced, this time through the charcoal tube.

(9) When condensation was complete, tap *l* was closed, and the apparatus from tap *f* on the manometer to the fall tube of the Sprengel pump (including the charcoal tube) exhausted. When this was complete, the difference between the combined pressures of the chlorine and marsh gas originally admitted and the pressure of the residual marsh gas gave the pressure due to the now condensed products of the reaction.

(10) The charcoal tube was then immersed in a tube of concentrated sulphuric acid, which was heated to  $300^{\circ}$ , and the methyl chloride evolved was pumped into the volumes,  $V + V_1$ , of the apparatus. It was found that the last traces of methyl chloride could be more easily removed if marsh gas was admitted three or four times to the charcoal tube from the reaction vessel, *C*. The increase in pressure observed when all the methyl chloride had passed off was therefore the pressure of the methyl chloride.

*Note.*—By removing the small condensing apparatus, it was possible to determine the weight of the higher chlorinated products of the reaction, namely, methylene dichloride, chloroform, and carbon tetrachloride.

*Experiments.*—Two experiments were made with marsh gas and chlorine in the proportions:

- (a) Marsh gas to chlorine = 2.80:1.0.
- (b) Marsh gas to chlorine = 1.075:1.0.

A third experiment was made with pure methane, which was prepared by the method described by Gladstone and Tribe (T., 1884, 45, 154) from a mixture of methyl iodide and methyl alcohol dropped on to the zinc-copper couple. The methane evolved was passed through a thin-walled vessel surrounded by a freezing mixture of ice and calcium chloride to remove any methyl iodide, then through two tubes containing concentrated sulphuric acid to remove alcohol, and finally collected over water. In this experiment, the proportions were:

- (c) Methane to chlorine = 1.12:1.0.

The results obtained in these experiments are given below:

Experiment.	Percentage of chlorine converted to methyl chloride.	Percentage of chlorinated marsh gas (methane in Expt. 3) converted to methyl chloride.
1	24.5	45.9
2	9.9	22.7
3	13.1	27.7

The results show that the proportion of chlorine converted to methyl chloride is too low to make the process an economical one for the preparation of methyl alcohol from methyl chloride prepared in this manner. No analysis was made of the easily con-

densified products of the reaction (methylene dichloride, chloroform, and carbon tetrachloride), but there is reason to believe that the amounts of these formed were substantially the same as those found by Bedford (*loc. cit.*) working with natural gas and chlorine in the proportion of 7:1. Bedford analysed the liquid product obtained, and found it to contain: methylene dichloride, 35; chloroform, 35; carbon tetrachloride, 5; chloroethanes, 20 per cent.; whilst the portion dissolved in the water contained: methylene dichloride, 61; chloroform, 28; carbon tetrachloride, 1.5; chloroethanes, 6 per cent.

*The Conversion of Methyl Chloride to Methyl Alcohol and Methyl Acetate.*

The following details have been very kindly supplied to me by Mr. D. L. Chapman:

It is well known that the hydrolysis of alkyl chlorides presents difficulties. E. Szarvasy (*J. Soc. Chem. Ind.*, 1916, **35**, 707) showed that methyl chloride can be slowly hydrolysed by heating it with alkali to 140° under a pressure of 20–24 atmospheres, and Lacy has shown that the time of hydrolysis is reduced by adding lime to the alkali. Hibbert and Brooks (*J. Amer. Chem. Soc.*, 1916, **38**, 1368) have also conducted an investigation on the preparation of amyl alcohol from amyl chloride under similar conditions. They have also investigated the preparation of the acetate by the action of amyl chloride on sodium acetate. The yields never exceeded 50 per cent., as the amyl alcohol and amyl acetate were both partly converted into amylene. Kaufler (Brit. Pat. 2779 and 3133 of 1913), using a porous and voluminous form of sodium acetate, converted the alkyl chlorides into acetates at a lower temperature than with the ordinary fused sodium acetate, and he recommends the addition of a small quantity of copper acetate to the sodium acetate, but Hibbert and Brooks found cuprous acetate ineffective as a catalyst.

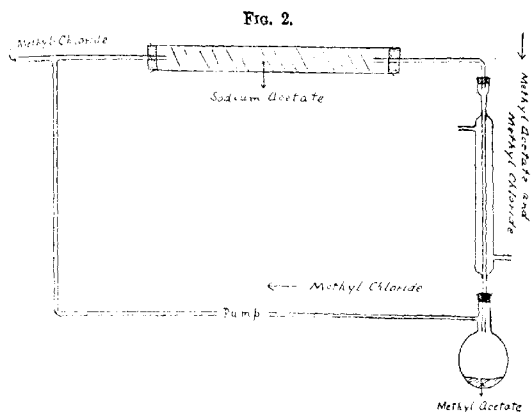
#### EXPERIMENTAL.

The methyl chloride was prepared by the method due to Groves. It was washed with sodium carbonate solution, scrubbed with concentrated sulphuric acid to remove methyl ether and the vapour of methyl alcohol, and then passed through the reaction tube heated in a gas furnace, which was maintained at a constant temperature by means of a thermoregulator.

*Preparation of Methyl Acetate.*—Using fused sodium acetate, methyl chloride begins to act at about 280°, and above 300° the

action is moderately rapid at the start, but soon falls off quickly, owing, no doubt, to the formation of a protective layer of sodium chloride on the surface of the sodium acetate. Moreover, if the reaction is continued, the liquid product contains only 89 per cent. of methyl acetate, 2.8 per cent. of the impurity being acetone, the remainder of the impurity not being identified. The residue left in the tube was found to be charred, but still contained some sodium acetate.

When sodium benzoate in the form of a very voluminous and porous network of crystals (prepared by adding the theoretical amount of sodium carbonate to a solution of benzoic acid, and then evaporating the solution of sodium benzoate) was used instead of



sodium acetate, it was found that the methyl chloride was converted quantitatively to methyl benzoate at 300–305°, the residue left in the tube being quite colourless. This was undoubtedly due to the porous condition of the sodium benzoate, and consequently suggested that the reaction, using sodium acetate, would also be complete if the sodium acetate were in a similar porous condition. A porous form of sodium acetate can be obtained by the action of glacial acetic acid on sodium carbonate, but to convert the whole of the carbonate into acetate, an excess of acetic acid must be used, and this is difficult to remove completely. It was found that a much more convenient method consisted in simply drying hydrated sodium acetate at 140°. Using the sodium acetate in this form, the methyl chloride was almost completely converted into methyl acetate. The apparatus used is depicted above.

The reaction tube was kept at  $290^{\circ}$  for four hours, and at  $295$ — $297^{\circ}$  for a further four hours. At the end of this time, methyl acetate was still slowly distilling over. It was found to be essential to stop the reaction when about 60—70 per cent. of the sodium acetate had been decomposed, and the unchanged acetate can be easily recovered from the residue by crystallisation or obtained as acetic acid by treating the residue with the calculated amount of hydrochloric acid and then distilling.

*Preparation of Methyl Alcohol.*—Preliminary experiments showed that below  $270^{\circ}$  methyl chloride and steam do not interact at all, whilst between  $270^{\circ}$  and  $320^{\circ}$  only small quantities of methyl alcohol and hydrogen chloride were produced. Consequently, attempts to hydrolyse methyl chloride by steam were discontinued. It was found, however, that methyl chloride acts on slaked lime and soda-lime at a convenient rate to give methyl alcohol, but with soda-lime some of the alcohol is lost, owing to the action of the alkali on it to give hydrogen and sodium formate. It was then found that, using the same apparatus as was used for the preparation of methyl acetate, but with slaked lime kept at  $300^{\circ}$  in place of the sodium acetate, the conversion of methyl chloride into methyl alcohol was also almost quantitative, a small loss being due to the formation of some methyl ether from the alcohol by loss of water.

#### *Conclusions.*

(1) The photochemical interaction between methane and chlorine never stops at the first possible stage to give only methyl chloride, but always continues further, giving a mixture of all the possible chlorinated products, in which methylene dichloride and chloroform predominate.

(2) Methyl chloride can be completely converted to methyl acetate by passing it over porous sodium acetate at  $290$ — $297^{\circ}$ .

(3) Methyl chloride can be almost completely converted to methyl alcohol by passing it over slaked lime at  $300^{\circ}$ .

My best thanks are due to Mr. D. L. Chapman for his advice and help during the progress of the work, and also to the Department of Scientific and Industrial Research for a grant enabling the work to be carried out.

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XXIV.—*Studies in the Resolution of Racemic Acids by Optically Active Alcohols. Part I. The Resolution of *r*-Tartaric Acid by *l*-Borneol.*

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THE possibility of using optically active alcohols for the resolution of racemic acids and, conversely, of active acids for the fission of racemic alcohols appears to have been first suggested by Frankland (Pasteur Memorial Lecture, T., 1897, **71**, 696), but efforts in this direction have generally met with little success. Thus, Frankland and Price (T., 1897, **71**, 253) found that resolution was not effected by crystallisation of *d*-amyl *r*-dibenzoylglycerate, whilst McKenzie (T., 1904, **85**, 384) was unable to resolve *l*-menthyl *r*-mandelate by repeated crystallisation. The latter substance has been the subject of extended investigation by Findlay and Miss Hickmans (T., 1907, **91**, 905), who found, by observation of the freezing-point curves, that *l*-menthyl *r*-mandelate exists in the liquid state at the temperature of its melting point, at which it is dissociated into its components to the extent of about 50 per cent., whilst, subsequently (T., 1909, **95**, 1386), they showed by measurement of its solubility that it cannot be resolved by crystallisation from aqueous or absolute alcohol at any temperature above  $-15^{\circ}$ . Similarly, McKenzie and Wren (T., 1907, **91**, 1222) observed that di-*l*-bornyl tartrate was not resolved into its diastereoisomerides by repeated crystallisation from methyl alcohol.

The only completely successful instance of a resolution of this type which appears to have been recorded up to the present is that described by Rupe and Häussler (*Annalen*, 1909, **369**, 324), who found that *l*-menthyl *l*- $\beta$ -phenylbutyrate crystallises from the product of the action of *l*-menthol on *r*- $\beta$ -phenylbutyryl chloride, and that it can be converted into *l*- $\beta$ -phenylbutyric acid by treatment with alcoholic potassium hydroxide solution. Subsequently, Rupe and Kerkovius (*Ber.*, 1912, **45**, 1398) showed that *l*-menthyl *l*- $\alpha$ - $\beta$ -diphenylpropionate can be separated into its diastereoisomerides by fractional crystallisation from alcohol, but they were unable to isolate the corresponding acids in a condition even approximating to optical purity on account of the great readiness with which racemisation occurred when the esters were hydrolysed with alcoholic alkali.

The esters which have been investigated in this manner are all

normal in type. A short time ago Wren and Still (T., 1917, 111, 513), during the course of an examination of the *l*-menthyl esters of the diphenylsuccinic acids, observed that, whilst *l*-menthyl hydrogen *r*-diphenylsuccinate is not resolved by crystallisation from light petroleum, its sodium salt could be partly resolved by crystallisation from water or by agitating its aqueous suspension with ether, whilst fission also occurred when the potassium salt was fractionally extracted with boiling ether. It therefore appeared possible that the salts of acid esters of racemic acids and optically active alcohols might lend themselves to purposes of resolution, and a series of experiments has been made in this direction. As acid, tartaric acid was selected both on account of its inherent stereochemical interest and ready availability. The choice of alcohol is much more restricted, since there are but few of these substances which can be obtained readily in suitable quantity and in a condition of optical purity; *l*-borneol and *l*-menthol naturally suggested themselves, and preference was accorded to the former, since it was considered that it would be more likely to yield well-crystallised esters, the behaviour of which could be studied in a variety of solvents.

The bulk of the requisite *l*-bornyl hydrogen *dl*-tartrate was prepared by mixing equal weights of the corresponding diastereoisomerides, which are conveniently prepared by the semi-hydrolysis of the appropriate normal esters, and are beautifully crystalline substances; under the conditions described in the experimental section, racemisation by alkali does not occur to any appreciable extent, since the acid esters obtained by hydrolysis are identical in all respects with those isolated as by-products in the esterification of the active acids with *l*-borneol.

The results of the investigation are somewhat unexpected, since it is found that *l*-bornyl hydrogen *dl*-tartrate is itself resolvable by crystallisation from every solvent which has been examined. The process has been carried to completion from chloroform, and potassium hydrogen *d*- and *l*-tartrates have been isolated in the pure state, whilst fission has also been shown to occur when water, benzene, toluene, or carbon tetrachloride is employed; in every case, *l*-bornyl hydrogen *d*-tartrate separates first. The sodium and barium salts, on the other hand, do not appear to be well adapted for resolution, although distinct evidence of the separation of the diastereoisomerides from aqueous solution has been obtained in each case. It is noticeable that the salts of *l*-bornyl hydrogen *l*-tartrate appear to be the more sparingly soluble, but the differences in solubility are less marked than in the case of the acid esters themselves.

## EXPERIMENTAL.

*Preparation of Di-l-bornyl d-Tartrate and of l-Bornyl Hydrogen d-Tartrate.*

An intimate mixture of finely-powdered *d*-tartaric acid (70 grams) and *l*-borneol (200 grams) was heated in an intermittent current of dry hydrogen chloride during sixteen hours at 120°; the product was dissolved in ether, and the ethereal solution washed with aqueous sodium carbonate (solution A). After removal of the solvent, the residue was distilled with steam to remove excess of *l*-borneol, and the crude ester was purified by crystallisation from rectified spirit until the specific rotation of successive crops remained constant. The yield of ester after one crystallisation was 140 grams.

*Di-l-bornyl d-tartrate* separates from slightly aqueous alcohol in small, colourless needles. It is freely soluble in cold ether, chloroform, acetone, toluene, carbon tetrachloride, or carbon disulphide, but less readily so in cold alcohol or light petroleum. It melts at 132.5–133.5°:

0.1598 gave 0.3993 CO<sub>2</sub> and 0.1318 H<sub>2</sub>O. C=68.1; H=9.2.

C<sub>24</sub>H<sub>38</sub>O<sub>6</sub> requires C=68.2; H=9.1 per cent.

The following observations of the specific rotation were made:

In chloroform solution:

$$l=2, c=2.0275, \alpha_D^{25} - 0.21^\circ, [\alpha]_D^{25} - 5.17^\circ.$$

In acetone solution:

$$l=2, c=2.275, \alpha_D^{25} - 0.26^\circ, [\alpha]_D^{25} - 5.71^\circ.$$

In benzene solution:

$$l=2, c=2.1605, \alpha_D^{25} + 0.15^\circ, [\alpha]_D^{25} + 3.46^\circ.$$

The aqueous-alkaline solution A (see above) was acidified and extracted with ether, whereby a small quantity of *l*-bornyl hydrogen *d*-tartrate was isolated, which, after being crystallised from toluene, melted at 158° and had  $[\alpha]_D^{25} - 6.05^\circ$  in ethyl-alcoholic solution; it was thus identical with the main bulk of the acid ester, which was prepared in the following manner. *Di-l-bornyl d-tartrate* (130 grams) was dissolved in a hot mixture of alcohol (250 c.c.) and water (130 c.c.), and a hot solution of the theoretical quantity of aqueous-alcoholic potassium hydroxide (1.856*N*, 167 c.c.) was rapidly added; the temperature of the mixture rose spontaneously to the boiling point, at which it was maintained for a few minutes, when hydrolysis was complete. The neutral solution was evaporated to remove alcohol, water was added, and the liberated borneol was separated by means of ether. The aqueous solution was acidified with hydrochloric acid and extracted with ether, whereby 55 grams of nearly



pure acid ester were isolated; the substance was crystallised from chloroform until successive crystallisations caused no change in the specific rotation of the product.

*l*-Bornyl hydrogen *d*-tartrate separates from boiling chloroform or toluene in shining leaflets. It is freely soluble in cold ethyl alcohol, acetone, or ether, moderately so in hot water, toluene, or chloroform, and very sparingly so in carbon disulphide, carbon tetrachloride, or light petroleum. It melts at 158–158.5°:

0.1600 gave 0.3451 CO<sub>2</sub> and 0.1122 H<sub>2</sub>O. C=58.8; H=7.8.

C<sub>14</sub>H<sub>22</sub>O<sub>6</sub> requires C=58.7; H=7.8 per cent.

The specific rotation was observed in ethyl alcohol and in acetone. In ethyl-alcoholic solution:

$l=2$ ,  $c=2.1805$ ,  $\alpha_D^{25} - 0.19^\circ$ ,  $[\alpha]_D^{25} - 5.7^\circ$ .

$l=2$ ,  $c=7.575$ ,  $\alpha_D^{25} - 0.99^\circ$ ,  $[\alpha]_D^{25} - 6.5^\circ$ .

In acetone solution:

$l=2$ ,  $c=2.3795$ ,  $\alpha_D^{25} - 0.06^\circ$ ,  $[\alpha]_D^{25} - 1.26^\circ$ .

Aqueous solutions of *l*-bornyl hydrogen *d*-tartrate are somewhat surprisingly sensitive to the presence of slight local excesses of alkali hydroxides; the alkali salts are therefore most conveniently prepared by gently warming aqueous solutions of calculated amounts of the acid ester and of the requisite alkali hydrogen carbonate.

Potassium *l*-bornyl *d*-tartrate separates from water, in which it is rather freely soluble, in aggregates of silky needles:

0.9980 \* lost 0.1055 at 105°. H<sub>2</sub>O=10.56.

C<sub>14</sub>H<sub>21</sub>O<sub>6</sub>K, 2H<sub>2</sub>O requires H<sub>2</sub>O=10.0 per cent.

0.2408 † gave 0.0630 K<sub>2</sub>SO<sub>4</sub>. K=11.74.

C<sub>14</sub>H<sub>21</sub>O<sub>6</sub>K requires K=12.05 per cent.

Sodium *l*-bornyl *d*-tartrate is less readily soluble in water than the corresponding potassium salt:

1.0024 \* lost 0.0960 at 105°. H<sub>2</sub>O=9.57.

C<sub>14</sub>H<sub>21</sub>O<sub>6</sub>Na, 2H<sub>2</sub>O requires H<sub>2</sub>O=9.56 per cent.

0.4873 † gave 0.1100 Na<sub>2</sub>SO<sub>4</sub>. Na=7.3.

C<sub>14</sub>H<sub>21</sub>O<sub>6</sub>Na requires Na=7.5 per cent.

#### *Preparation of Di-l-bornyl l-Tartrate and of l-Bornyl Hydrogen l-Tartrate.*

The requisite *l*-tartaric acid was prepared by the resolution of *r*-tartaric acid by cinchonine in aqueous solution in accordance with the directions of Marckwald (*Ber.*, 1896, **29**, 42); for the present purposes, the isolation of the free acid was unnecessary, and it was

\* Air-dried.

† Dried at 105–110°.

found more advantageous to separate the sparingly soluble potassium hydrogen salt. This was converted into di-*l*-bornyl *l*-tartrate by *l*-borneol in the presence of hydrogen chloride in the same manner as has been described for the corresponding *d*-ester. The crude normal ester was purified by crystallisation from alcohol and finally from light petroleum.

*Di-l-bornyl l-tartrate* separates from light petroleum in large, ill-defined, hexagonal plates; it is freely soluble in the boiling, sparingly so in the cold, solvent. It dissolves readily in cold chloroform, benzene, toluene, or acetone, and moderately readily in cold ethyl alcohol. It is more readily soluble than its diastereoisomeride in all the solvents investigated. It melts at 118–118.5°:

0.1544 gave 0.3860 CO<sub>2</sub> and 0.1272 H<sub>2</sub>O. C=68.2; H=9.2.

C<sub>24</sub>H<sub>36</sub>O<sub>6</sub> requires C=68.2; H=9.1 per cent.

The specific rotation was observed in the following solvents:

In chloroform solution:

$$l=2, c=2.520, \alpha_D^{15} = -3.60^\circ, [\alpha]_D^{15} = -71.4^\circ.$$

In benzene solution:

$$l=2, c=2.416, \alpha_D^{15} = -3.75^\circ, [\alpha]_D^{15} = -77.6^\circ.$$

In acetone solution:

$$l=2, c=2.5405, \alpha_D^{15} = -2.90^\circ, [\alpha]_D^{15} = -71.3^\circ.$$

The mean of the specific rotations of di-*l*-bornyl *d*-tartrate (–5.17°) and di-*l*-bornyl *l*-tartrate (–71.4°) when dissolved in chloroform is –38.3°, a value which is in good agreement with the figure (–38.5°) found by McKenzie and Wren (T., 1907, **91**, 1221) by direct observation with di-*l*-bornyl *r*-tartrate.

*l*-Bornyl hydrogen *l*-tartrate was isolated in small amount as a by-product of the preparation of the normal ester; it melted at 130.5–131° and had  $[\alpha]_D^{15} = 52.2^\circ$  ( $c=2.6608$ ) in ethyl-alcoholic solution. It was identical in all respects with the bulk of the hydrogen ester, which was prepared by the semi-hydrolysis of the normal ester in a manner similar to that described for the diastereoisomeride.

*l*-Bornyl hydrogen *l*-tartrate separates from benzene in shining leaflets; it dissolves readily in the boiling, sparingly in the cold, solvent. It is freely soluble in cold chloroform, alcohol, acetone, or hot water, moderately so in boiling carbon disulphide or carbon tetrachloride, and sparingly so in boiling light petroleum (b. p. 60–80°). In general, it is very noticeably more readily soluble in all solvents than is its diastereoisomeride. It melts at 130.5–131°:

0.1637 gave 0.3519 CO<sub>2</sub> and 0.1116 H<sub>2</sub>O. C=58.6; H=7.6.

C<sub>14</sub>H<sub>22</sub>O<sub>6</sub> requires C=58.7; H=7.8 per cent.

The specific rotation was determined in ethyl-alcoholic solution:

$$l=2, c=2.985, \alpha_D^{15} - 2.47^\circ, [\alpha]_D^{15} - 51.7^\circ.$$

*l*-Bornyl hydrogen *dl*-tartrate was prepared by dissolving equal weights of the diastereoisomerides in acetone and rapidly removing the solvent:

0.1543 gave 0.3316 CO<sub>2</sub> and 0.1057 H<sub>2</sub>O. C=58.6; H=7.7.

C<sub>14</sub>H<sub>22</sub>O<sub>6</sub> requires C=58.7; H=7.8 per cent.

The specific rotation was observed in ethyl-alcoholic solution:

$$l=2, c=2.7792, \alpha_D^{15} - 1.57^\circ, [\alpha]_D^{15} - 28.2^\circ.$$

The mean of the values observed for *l*-bornyl hydrogen *d*-tartrate and *l*-bornyl hydrogen *l*-tartrate under closely similar conditions is  $-28.7^\circ$ .

*Resolution of l-Bornyl Hydrogen dl-Tartrate by Crystallisation from Chloroform.*

Equal weights of *l*-bornyl hydrogen *d*-tartrate and *l*-bornyl hydrogen *l*-tartrate (20 grams of each) were mixed and dissolved in boiling chloroform (150 c.c.); on cooling the solution, crystallisation occurred after some time. The mixture was allowed to remain at the ordinary temperature for about eight hours, after which it was filtered. The crystalline crop weighed 9.6 grams and had  $[\alpha]_D - 9.8^\circ$  in ethyl-alcoholic solution. It was again crystallised from the same solvent (90 c.c.), whereby 5 grams of material were obtained which melted at  $157-158.5^\circ$  and had  $[\alpha]_D^{15} - 7.2^\circ$  in alcoholic solution. A further crystallisation yielded pure *l*-bornyl hydrogen *d*-tartrate, which was identified by analysis (Found, C=58.8; H=7.7. Calc., C=58.7; H=7.8 per cent.), by melting point,  $157.5-158^\circ$ , both alone and when mixed with an approximately equal amount of synthetic *l*-bornyl hydrogen *d*-tartrate and by determination of the specific rotation in ethyl-alcoholic solution:

$$l=2, c=2.392, \alpha_D^{15} - 0.32^\circ, [\alpha]_D^{15} - 6.6^\circ.$$

Elimination of the *l*-bornyl group was readily effected by the action of a slight excess of aqueous potassium hydroxide solution (0.931*N*) on the aqueous suspension of the ester. On addition of alkali, the odour of borneol became immediately very apparent. After remaining for about two hours at the ordinary temperature the mixture was gradually heated on the water-bath. The precipitated borneol was removed by filtration, and the filtrate was extracted with ether to complete the elimination of the borneol. The aqueous solution was then treated with standard hydrochloric acid in the quantity necessary for the formation of potassium

hydrogen tartrate, when the latter salt immediately separated; it was purified by crystallisation from water and dried in a vacuum over calcium chloride (0.2038 neutralised 10.95 c.c. *N*/10-potassium hydroxide solution. Calc., 10.83 c.c. 0.1681 gave 0.0775  $K_2SO_4$ .  $K=20.7$ . Calc.,  $\bar{K}=20.8$  per cent.).

As the sparing solubility of potassium hydrogen tartrate in water does not render it a suitable substance for polarimetric analysis it was dissolved in the quantity of aqueous *N*-potassium hydroxide necessary to form the normal salt and the solution was diluted to the mark with water.

3.113 Grams of potassium hydrogen tartrate, dissolved in potassium hydroxide and the solution made up to 25 c.c. with water, had  $[\alpha]_D^{20} + 8.48^\circ$  in a 2-dcm. tube, when  $[\alpha]_D^{15} + 28.3^\circ$ . (The concentration of the solution expressed in terms of the normal tartrate is 14.972 grams per 100 c.c.). This value agrees well with the data recorded in the literature for normal potassium *d*-tartrate; thus, Schütt (*Ber.*, 1888, **21**, 2586) gives  $[\alpha]_D^{20} + 28.61^\circ$  for  $c=19.23$  and  $[\alpha]_D^{20} + 28.01^\circ$  for  $c=9.62$ , whilst Thomsen (*J. pr. Chem.*, 1886, [ii], **34**, 89) found  $[\alpha]_D^{15} + 29.02^\circ$  for  $c=20.38$  and  $+28.34^\circ$  for  $c=9.62$ .

The filtrate obtained from the first crystallisation of the *l*-bornyl hydrogen *dl*-tartrate (see above) was allowed to evaporate spontaneously, whereby 29.3 grams of material were obtained which had  $[\alpha]_D - 33.7^\circ$  in ethyl-alcoholic solution. It was crystallised from boiling chloroform (50 c.c.), when the crop which separated (9 grams) had  $[\alpha]_D - 12.17^\circ$ , whilst the product obtained by evaporation of the filtrate weighed 20 grams and had  $[\alpha]_D - 40.0^\circ$  in alcohol. The latter was decomposed with aqueous potassium hydroxide solution and the potassium salts were converted into the mixture of *r*- and *l*-tartaric acids. The bulk of the former was removed by cautious crystallisation of the mixed acids from a small quantity of water. The acids contained in the filtrate were transformed into their potassium hydrogen salts, which were subsequently crystallised from water, ultimately yielding a small amount of potassium hydrogen *l*-tartrate in a state of purity (Found,  $K=20.7$ . Calc.,  $K=20.8$  per cent.).

0.6315 Gram dissolved in the requisite quantity of *N*-potassium hydroxide solution and diluted to 25 c.c. with water had  $\alpha_D - 1.65^\circ$  at  $16^\circ$  in a 2-dcm. tube, whence  $[\alpha]_D^{16} - 27.2^\circ$ . (The concentration of the solution expressed as normal tartrate is 3.036 grams per 100 c.c.). By extrapolation from Schütt's data (*loc. cit.*) the pure anhydrous potassium *l*-tartrate has  $[\alpha]_D^{20} - 27.4^\circ$  at this concentration.

*Experiments on the Resolution of l-Bornyl Hydrogen dl-Tartrate from Solvents other than Chloroform.*

*From Carbon Tetrachloride.*—Equal weights of the diastereoisomerides (0.8727 gram in each case) were mixed and dissolved in boiling carbon tetrachloride (520 c.c.). The solution was allowed to cool to the ordinary temperature; the crystals which separated had  $[\alpha]_D -26.5^\circ$ , whilst the material left on evaporation of the mother liquor had  $[\alpha]_D -34.2^\circ$  in ethyl-alcoholic solution.

*From Water.*—The mixed esters (1.7524 grams) were dissolved in hot water (30 c.c.); nothing separated from the cold solution, which was therefore seeded with a minute quantity of the *d*-ester, when a small crop slowly formed. The specific rotations of the crystals and of the portion which remained in solution were  $-6.9^\circ$  and  $-31.1^\circ$  respectively.

*From Benzene.*—1.9226 Grams of the mixed esters were dissolved in boiling benzene (40 c.c.); the cold solution deposited 1.6 grams of substance, which was further crystallised from 80 c.c. of the solvent. 1.05 Grams of material, having  $[\alpha]_D -19.9^\circ$  in alcohol, were obtained, whilst the residues left on evaporation of the successive filtrates had  $[\alpha]_D -34.9^\circ$  and  $-36.5^\circ$  respectively.

*From Toluene.*—The solution of the mixed esters (1.8214 grams) in hot toluene (30 c.c.) deposited 1.57 grams of material, which was recrystallised from 100 c.c. of the solvent. The second crop had  $[\alpha]_D -25.0^\circ$  in ethyl-alcoholic solution, whilst the material obtained from the united mother liquors had  $[\alpha]_D -35.5^\circ$ .

*Resolution of l-Bornyl Hydrogen dl-Tartrate by Crystallisation of its Salts.*

*Sodium Salt.*—1.8472 Grams of the *dl*-ester were suspended in warm water (24 c.c.) and treated with sodium hydrogen carbonate in slight excess; a clear solution was readily obtained, from which crystals separated on cooling. The separated salt and that contained in the filtrate were converted into the hydrogen esters and polarimetrically examined in ethyl-alcoholic solution, when the values  $-29.4^\circ$  and  $-28.0^\circ$  respectively were observed for the specific rotations.

*Barium Salt.*—Equal weights of the diastereoisomerides (0.9571 gram in each case) were dissolved in water, and the solution was neutralised by the cautious addition of dilute aqueous barium hydroxide. The dense precipitate was dissolved in hot water (2 litres) and the solution was allowed to cool, when a crystalline crop gradually separated. The specific rotations of the hydrogen esters

obtained from the crop and filtrate were  $-29.3^{\circ}$  and  $-26.8^{\circ}$  respectively.

In the experiments which have just been described, the requisite *dl*-ester was obtained by mixing equal weights of the *d*- and *l*-esters. Preliminary experiments indicated, as was to be expected, that resolution can equally be effected starting from *r*-tartaric acid. Thus, in one case, the latter acid was completely esterified with *l*-borneol and the *l*-bornyl *r*-tartrate was treated with half the quantity of potassium hydroxide necessary for complete hydrolysis; the crude *l*-bornyl hydrogen *dl*-tartrate obtained in this way was repeatedly crystallised from benzene, when the specific rotations of the second, third, and fourth crops were  $-27.0^{\circ}$ ,  $-23.3^{\circ}$ , and  $-21.1^{\circ}$  respectively. It is hoped to give a more complete account of this aspect of the case when the behaviour of the esters of racemic dibasic acids and optically active alcohols on subjection to partial hydrolysis has been more fully investigated.

The authors desire to express their thanks to the Research Fund Committee of the Royal Society for a grant which has defrayed part of the cost of the investigation.

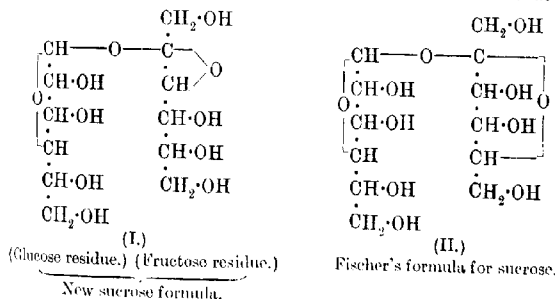
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## XXV.—*The Constitution of the Disaccharides.* *Part IV. The Structure of the Fructose Residue in* *Sucrose.*

By WALTER NORMAN HAWORTH.

A NEW constitutional formula for sucrose (I) was proposed in a former communication in this series, where it was shown that the



fructose residue contained in sucrose could not possess the structure generally assigned to it (Haworth and Law, T., 1916, **109**, 1314).

The data on which this conclusion was based may be summarised as follows: (1) On hydrolysis with dilute acids, octamethyl sucrose does not show the phenomenon of "inversion," as does sucrose, whereas, in conformity with the usual experience, the cleavage of the methylated disaccharide ought to give rise to a molecular mixture of tetramethyl glucose and tetramethyl fructose which would be predominantly levorotatory.

(2) This unexpected result was traceable to the fructose residue which, differing in structure from ordinary fructose, displayed a pronounced dextrorotation.

(3) The crystalline tetramethyl fructose (IV), isolated by Purdie and Paul (T., 1907, **91**, 296) during their study of the methylation of methyl fructoside, showed a specific rotation of  $[\alpha]_D -121^\circ$  in aqueous solution, whilst the corresponding product derived from the hydrolysis of octamethyl sucrose by Haworth and Law (*loc. cit.*) was a liquid which distilled easily, but did not crystallise on nucleation with a specimen of Purdie and Paul's compound. Moreover, the new form of tetramethyl fructose was unstable towards permanganate and behaved uniformly as a sugar derivative of the  $\gamma$ - or supposed ethylene-oxide type.

Opportunity has again been taken to isolate this new form of tetramethyl fructose and to submit it to further constitutional study. The isolation of this compound in a state of purity from the products of hydrolysis of octamethyl sucrose was attended with much experimental difficulty. This was due to its occurrence along with the isomeric tetramethyl glucose, since the latter distils at approximately the same temperature as the methylated fructose fragment.

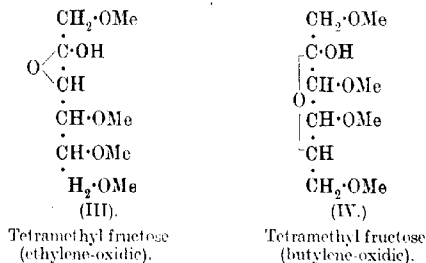
In the present series of experiments it has been found that the difficulty formerly experienced in separating the cleavage products vanishes if heptamethyl sucrose is substituted for the completely methylated biose in a parallel experiment. The advantage conferred by the use of heptamethyl sucrose is attributable to the nature of its scission products, which distil at temperatures sufficiently remote from each other to admit of easy separation by fractional distillation. The partly methylated biose was obtained by methylating sucrose in alkaline solution with methyl sulphate (Haworth, T., 1915, **107**, 12), and this has been shown to be a pure chemical individual, in which the fructose constituent is fully methylated, but only three methyl groups are present in the glucose component.

When heptamethyl sucrose was hydrolysed with 0.4 per cent. hydrochloric acid at 60° for six and a-half hours the specific rotation

diminished from  $[\alpha]_D + 64.3^\circ$  to  $+52^\circ$ , and at the latter value remained constant. The products of this change consisted of a molecular mixture of a trimethyl and a tetramethyl hexose, which was easily separable by distillation at the Gaebe pump. The first fraction distilled as a colourless, mobile liquid at  $110\text{--}112^\circ/0.35$  mm., having  $n_D$  1.4545, and gave analytical results corresponding with a tetramethyl hexose. A second fraction was collected as a viscid syrup, boiling at  $170^\circ/0.43$  mm., showing  $n_D$  1.4755, and analysis proved it to be a trimethyl hexose. The amounts of both fractions were approximately equal.

Clearly it was of importance to decide which of these individual fractions represented the glucose or fructose residue in the original sucrose. This point was established by submitting the trimethyl hexose to further methylation, when it was converted into a crystalline substance melting at  $83^\circ$ , showing  $[\alpha]_D + 84^\circ$ , and identical with tetramethyl glucose (compare Haworth and Law, *loc. cit.*, p. 1324), a result which afforded ample proof that the trimethyl hexose was a glucose derivative. Consequently, it follows that the tetramethyl hexose having the lower boiling point represented the fructose residue in sucrose.

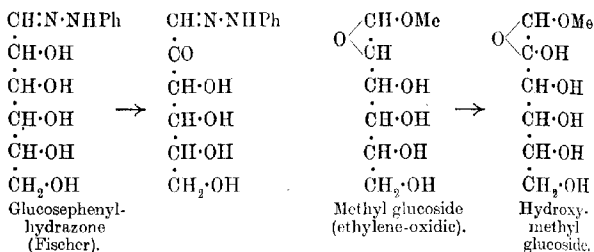
Attention has been focussed in the course of the present investigation on this specimen of tetramethyl fructose. In the previous communication on this subject (*loc. cit.*) an approximation only could be made as to the probable specific rotation of this compound in aqueous solution, and the value was tentatively given as  $[\alpha]_D + 29.3^\circ$ . The correct value, determined experimentally for the first time, differs only slightly from this anticipated result, and is now recorded as  $[\alpha]_D + 31.7^\circ$ . The substance is very unstable towards permanganate, and conforms to the new type of hexoses which have been provisionally named ethylene-oxide sugars. Further, the constitution previously assigned to the new variety of tetramethyl fructose (III) has been subjected to close experimental scrutiny:



In allocating this structural formula (III) to the fructose residue

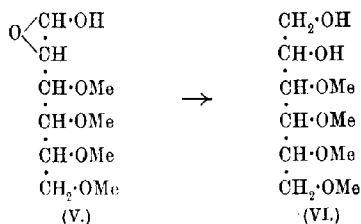


in sucrose the only basis on which one could proceed was the valuable group of facts recorded by Irvine, Fife, and Hogg during their investigation of the new variety of tetramethyl glucose (V), described as a  $\gamma$ -sugar (T., 1915, 107, 524). These authors showed that a derivative of  $\gamma$ -glucose examined by them showed a remarkable capacity to increase its oxygen content to the extent of one atomic proportion during methylation with silver oxide and methyl iodide. Surprising though this behaviour may be, it finds a parallel in the oxidation of glucose with phenylhydrazine which gives rise to the glucosazone. It is established that in the latter case the oxidation change effects removal of the hydrogen atoms attached to the second carbon atom from the reducing end of the hexose chain. The analogy which has been drawn between the two reactions leads to the suggestion that in both cases oxidation is confined to the groups associated with the carbon atom which adjoins the reducing group:



The above formulæ are given in this simple form for the sake of clearness; it will be recognised that the two products of oxidation indicate only intermediate stages of the reactions which have been studied. The main point is, that if the analogy be admitted, the ethylene-oxide form of methyl glucoside is the only one that can hold for the new type of sugar derivative.

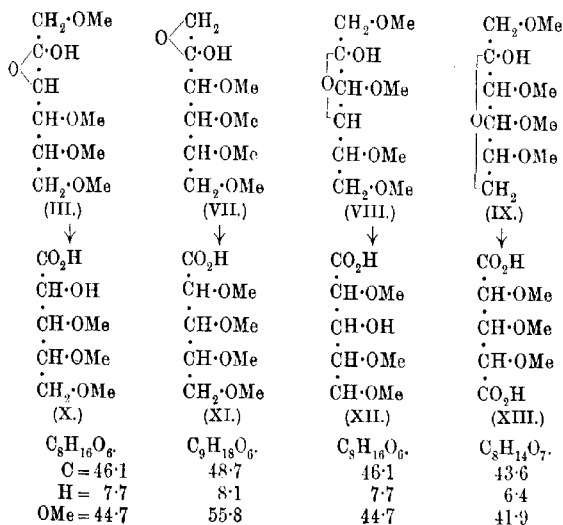
In order to furnish a proof of this structural arrangement, Irvine, Fife, and Hogg (*loc. cit.*) submitted a derivative of the new type of  $\gamma$ -sugar, namely, tetramethyl  $\gamma$ -glucose (V), to (a) reduction,



(b) oxidation. The product of reduction was a tetramethyl sorbitol (VI), which showed optical exaltation in the presence of boric acid, and thus, in the light of Böeseken's recent work (*Ber.*, 1913, **46**, 2612), the compound contained two hydroxyl groups attached to neighbouring carbon atoms, a result which affords strong support to the ethylene-oxide formula of the sugar.

On the other hand, oxidation of the sugar (V) with permanganate gave rise to a unimolecular lactone, the formation of which would appear to be precluded if the ethylene-oxide structure were adopted as above. Whilst, therefore, this mode of representation was provisionally proposed for the new or  $\gamma$ -sugars, it was recognised that other interpretations were possible.

Consequently, in the special case under review, namely, that of the fructose residue isolated from heptamethyl sucrose, it was considered of first importance to provide some additional experimental basis on which the structure assigned to this compound could rest. Apart from the butylene-oxide form of tetramethyl fructose (IV) which has been definitely characterised, there would appear to be no fewer than four possible formulæ by which the tetramethyl fructose isolated in the course of the present investigation may be represented; these are given as the following, and for the sake of comparison the oxidation products to which they may be expected to give rise are printed below in the vertical column:



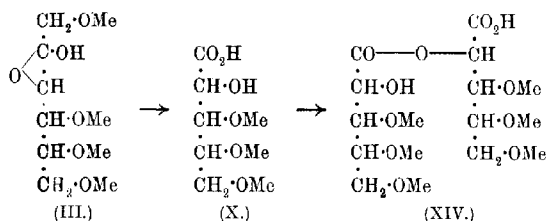
The choice of oxidising agent, namely, dilute nitric acid, was determined by the fact that oxidation of a sugar of the formula (IX), if effected with bromine water, would leave a primary alcohol group exposed, whilst nitric acid would oxidise both the reducing and primary alcohol groups. On submitting the specimen of tetramethyl fructose to oxidation with nitric acid at  $60^{\circ}$ , a viscid liquid was formed which distilled at  $190\text{--}200^{\circ}/1.8\text{ mm.}$ , and analysis gave  $C=48.17$ ;  $H=7.43$ ;  $OMe=43.4$ . Such a result is not in agreement with any of the figures quoted above, although it approximates closely to those required for dehydration of two molecular proportions of  $C_8H_{16}O_6$ , namely,  $C_{16}H_{30}O_{11}$ , which requires  $C=48.24$ ;  $H=7.54$ ;  $OMe=46.7$  per cent. A determination of molecular weight by the cryoscopic method gave 354; that required by the bimolecular anhydride is 398, whilst the unimolecular formula require approximately half this value.

Inspection of the formula (X) will indicate that this represents an  $\alpha$ -hydroxy-acid, and may be referred to lactic acid as a type. It is well known that lactic acid undergoes conversion into an anhydride or semi-lactide, either by heating at  $130\text{--}140^{\circ}$ , or spontaneously at the ordinary temperature in a dry atmosphere. The formula (XII) admits of the possibility of the formation of a unimolecular  $\beta$ -lactone, since Nef has shown that mannono- $\beta$ -lactone is easily formed, but passes into aqueous solution as regenerated mannonic acid (*Annalen*, 1914, **403**, 204). Nef also mentions the existence of bimolecular  $\alpha$ -lactones, by which is meant substances analogous to the semi-lactide from lactic acid, which has already been quoted. On the other hand, formulæ (XI) and (XIII) do not admit of the possibility of dehydration except by the ordinary process of preparing acid anhydrides.

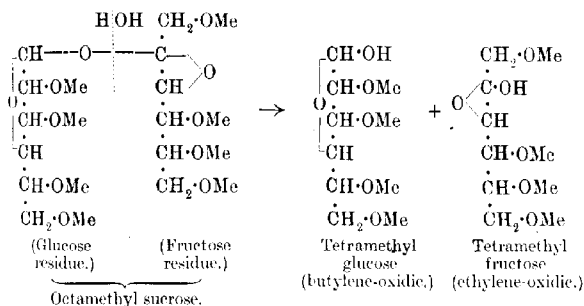
It was ascertained by analysis that, in the particular experiment under review, when the product derived from the oxidation of the tetramethyl fructose was isolated from aqueous solution by evaporation of the solvent, anhydride formation had already occurred, and a consideration of all the possible formulæ leads to the conclusion that this could only take place with an  $\alpha$ -hydroxy-acid. It will be remembered that the oxidation product was found to possess the formula  $C_{16}H_{30}O_{11}$ , and is thus bimolecular. Moreover, the compound was acid towards litmus, and when titrated with alkali it behaved as an acid until about half the total alkali required for complete neutralisation had been added. From this point onward the substance exhibited all the properties of a lactone, absorption of additional alkali taking place with extreme slowness. The final result corresponded exactly with the requirements for a semi-

lactide (XIV) of the formula  $C_{16}H_{30}O_{11}$ , and full details will be found in the experimental part.

From these considerations it will be clear that the oxidation product must have been formed from an acid of formula (X), which in turn can only represent a product of degradation of a tetramethyl fructose having the formula (III):



This result furnishes valuable evidence in support of the constitutional formula (I) for sucrose, advanced in an earlier communication by Haworth and Law (this series, Part I), and the hydrolysis of octamethyl sucrose therein described may now be formulated:



A similar representation would apply to the hydrolytic cleavage of heptamethyl sucrose, except that in this case a butylene-oxide form of trimethyl glucose is obtained as the glucose constituent.

An explanation of the observed facts that, when free sucrose is hydrolysed, glucose and ordinary levorotatory fructose are found as the products, is given in Part I. of this series. It is there stated that although the ethylene-oxide form of fructose must first be produced, the hydrolysis is accompanied by a supplementary structural change involving the transformation of the fructose residue at the moment of cleavage into a butylene-oxide form. Such supple-

mentary changes are inhibited if the hydroxyl groups in sucrose are protected by methyl groups.

Although the additional evidence here contributed as to the structure of sucrose appears capable of no simple explanation other than that now offered, the constitution of the new form of tetramethyl fructose is being further investigated in view of the importance of the issues.

#### EXPERIMENTAL.

##### *Hydrolysis of Heptamethyl Sucrose.*

Heptamethyl sucrose (28 grams), prepared by the method already described (Haworth, T., 1915, **107**, 12), was dissolved in 450 c.c. of 0.4 per cent. aqueous hydrochloric acid and the mixture heated in a water-bath maintained at 60°. Polarimetric readings were taken from time to time, and hydrolysis was complete in six and a-half hours:

	Time.	<i>l.</i>	$\alpha_D$ .	$[\alpha]_D$ .
5 minutes	.....	2-dem.	+8.0°	+64.3°
1 hour	.....		7.0	
1½ hours	.....		6.46	
3 "	.....		6.76	
6½ "	.....		6.74	+54.0

At this stage the acid was neutralised with barium carbonate, and the solution filtered and evaporated under diminished pressure in presence of a trace of barium carbonate. A syrupy residue remained, which was contaminated with barium salts. The product was dissolved in absolute alcohol, filtered to remove mineral matter, and the solvent distilled. A further treatment with ether served to remove the whole of the suspended salts. Thereafter the residue was submitted to fractional distillation at the Gaede pump.

Nearly half the total product distilled as a colourless, mobile liquid at 110—120°/0.35 mm., whilst the remainder was collected at 154—170°/0.6 mm. On repeated refractionation of each portion two main fractions were obtained:

1. . . . b. p. 110—112°/0.32 mm.  $n_D$  1.4545.
2. . . . b. p. 168—170°/0.43 mm.  $n_D$  1.4755.

The latter substance was a viscid syrup, which failed to give an osazone on treatment with phenylhydrazine. On analysis it was shown to be a trimethyl hexose:

0.1206 gave 0.2149 CO<sub>2</sub> and 0.0888 H<sub>2</sub>O. C=48.60; H=8.19.

0.1284 gave, by Zeisel's method, 0.3988 AgI. OMe=41.0.

C<sub>6</sub>H<sub>9</sub>O<sub>5</sub>(OMe)<sub>3</sub> requires C=48.65; H=8.11; OMe=41.9 per cent.

This trimethyl hexose was submitted to further methylation by

methyl iodide and silver oxide. The product was thereafter hydrolysed with 8 per cent. hydrochloric acid at  $100^{\circ}$  for three hours in order to remove the glucosidic group and obtain the tetramethyl hexose. The latter was isolated in the usual way, and was found to consist of a liquid which quickly crystallised. Recrystallisation of the solid from light petroleum yielded characteristic prismatic needles, which were easily identified as tetramethyl glucose, melting at  $83^{\circ}$ , and showing no depression in melting point when mixed with a specimen of this sugar isolated on a previous occasion (T., 1916, 109, 1324). The specific rotation was  $[\alpha]_D +84^{\circ}$  in equilibrium in water.

Since tetramethyl glucose of the butylene-oxide form was isolated as the result of this experiment, there could be no doubt that the trimethyl hexose distilling at the higher temperature in fraction (2) was a trimethyl glucose of the normal type. This showed  $[\alpha]_D +55.7^{\circ}$  in methyl alcohol and  $+56.0^{\circ}$  in aqueous solution, and its further study will form the subject of a future communication.

#### A New Form of Tetramethyl Fructose (III).

The first fraction distilling at  $110-112^{\circ}/0.32$  mm. was also found to boil at  $154^{\circ}/13$  mm. It decolorised permanganate readily, and behaved generally as a  $\gamma$ -sugar. The following analytical results were obtained:

0.2220 gave 0.4141  $\text{CO}_2$  and 0.1700  $\text{H}_2\text{O}$ . C=50.87; H=8.51.

0.1420 „ 0.5430 AgI. OMe=50.3.

$\text{C}_6\text{H}_5\text{O}_2(\text{OMe})_4$  requires C=50.85; H=8.47; OMe=52.5 per cent.

The specific rotation of the sugar was determined.

Solvent.	$[\alpha]_D$ .
Water.....	$+31.7^{\circ}$ (final reading)
Methyl alcohol .....	$+21.3^{\circ}$

When the aqueous solution was catalysed with a trace of hydrochloric acid, the specific rotation increased to  $+32.6^{\circ}$ .

*Oxidation with Nitric Acid.*—The tetramethyl fructose (4.75 grams) was oxidised by heating with dilute nitric acid (D 1.2) at  $60^{\circ}$  for five hours. The water and most of the nitric acid were removed by vacuum distillation at low temperature, and the residue was treated successively with absolute alcohol and ether, followed by distillation of the solvent and continued heating in the vacuum of the Gaede pump until the whole of the nitric acid was removed.

In a preliminary attempt to purify the residual syrup it was dissolved in ether and shaken in a separating funnel with small quantities of water. There remained in the ethereal layer about one-fifth of the original amount of the syrup, and after drying and

removal of solvent this small residue was dried in a stream of air in a vacuum, when it gave the following analytical results:

0.1550 gave 0.2754  $\text{CO}_2$  and 0.1076  $\text{H}_2\text{O}$ .  $\text{C}=48.45$ ;  $\text{H}=7.71$ .

$\text{C}_{16}\text{H}_{30}\text{O}_{11}$  requires  $\text{C}=48.24$ ;  $\text{H}=7.54$  per cent.

The portion remaining in the aqueous layer was now extracted with much ether and the solvent removed by distillation. The residue was dried by heating at  $100^\circ$  in the vacuum of the Gaede pump, and at this stage a sample was removed for analysis:

0.1803 gave 0.3154  $\text{CO}_2$  and 0.1233  $\text{H}_2\text{O}$ .  $\text{C}=47.71$ ;  $\text{H}=7.59$ .

The syrup was then distilled, when it was observed that very little decomposition occurred. A small first fraction was collected as an amber-coloured syrup distilling at  $185\text{--}190^\circ/1.8$  mm., and a large second fraction was obtained, boiling at  $190\text{--}200^\circ/1.8$  mm. and having  $n_D=1.4575$ . The first fraction was analysed as follows:

0.1236 gave 0.2210  $\text{CO}_2$  and 0.0829  $\text{H}_2\text{O}$ .  $\text{C}=48.76$ ;  $\text{H}=7.45$ .

The second fraction gave the figures:

0.1042 gave 0.1841  $\text{CO}_2$  and 0.0697  $\text{H}_2\text{O}$ .  $\text{C}=48.17$ ;  $\text{H}=7.43$ .

0.1092 „ 0.3590 Agl.  $\text{OMe}=43.4$ .

$\text{C}_{10}\text{H}_{12}\text{O}_5(\text{OMe})_6$  requires  $\text{C}=48.24$ ;  $\text{H}=7.54$ ;  $\text{OMe}=46.7$  per cent.

This corresponds with an anhydro-acid (XIV) or semi-lactide,  $\text{C}_{16}\text{H}_{30}\text{O}_{11}$ . The substance appeared to be hygroscopic, and quickly absorbed water from a moist atmosphere.

During the titration with  $N/10$ -sodium hydroxide the syrupy oxidation product behaved at first as an acid, and finally as a lactone. Phenolphthalein was used as indicator. 0.1192 Gram was dissolved in water and titrated with  $N/10$ -sodium hydroxide. The alkali was rapidly absorbed until 2.9 c.c. had been added; thereafter additional alkali was absorbed with extreme slowness at the ordinary temperature. On adding in all 10 c.c. and heating under reflux for a quarter of an hour, the cooled solution was neutralised with  $N/10$ -sulphuric acid and required 3.85 c.c. The total alkali which had combined with the compound was therefore 6.15 c.c. The theoretical amount required for an anhydro-acid,  $\text{C}_{16}\text{H}_{30}\text{O}_{11}$ , is 5.98 c.c.

A determination of molecular weight in benzene solution was carried out by the cryoscopic method, when the values found were 354.1 and 343.5. The anhydro-acid,  $\text{C}_{16}\text{H}_{30}\text{O}_{11}$ , requires  $\text{M.W.}=398$ .

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,  
UNIVERSITY OF ST. ANDREWS.

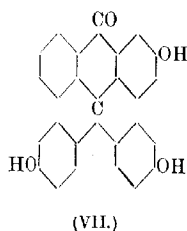
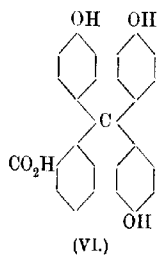
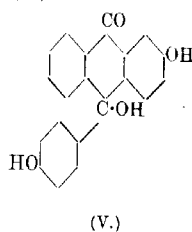
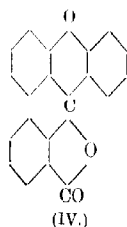
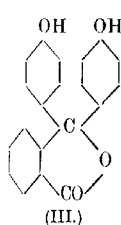
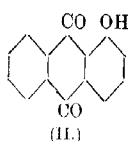
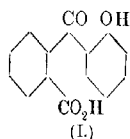
[Received, February 2nd, 1920.]

XXVI.—*Phthaleins and Fluorans.*

By MAURICE COPISAROW.

THE object of this investigation was the study of the constitution and conditions of formation of some members of the phthalein and fluoran series. Whilst certain phenols, such as resorcinol and pyrogallol, react with phthalic anhydride in the absence of any dehydrating agent, in most other cases some such agent is required for the condensation to take place. These condensing agents, in conjunction with the experimental conditions, influence not only the yield, but also the character of the products. In most cases, the formation of phthaleins (III) is accompanied by the production of substances belonging to the *o*-ketonic acid (I) (Deichler and Weizmann, *Ber.*, 1903, **36**, 547; Copisarow and Weizmann, *T.*, 1915, **107**, 878), hydroxyanthraquinone (II), and fluoran (IV) series.

It is probable that when aluminium chloride is employed as a condensing agent, the products just quoted are accompanied





by small quantities of substances belonging to the phenyl-oxanthranol (V), tetraphenylmethane-*o*-carboxylic acid (VI), and diphenylanthrone (VII) series (Copisarow, T., 1917, **111**, 10).

On replacing phthalic anhydride by phthalyl chloride, isophthaleins or phenolic esters of phthalic acid are formed (Baeyer, *Ber.*, 1871, **4**, 659; Meyer, *Ber.*, 1891, **24**, 1414; 1893, **26**, 204; 1895, **28**, 431; Pawlewski, *Ber.*, 1895, **28**, 108, 2360; Limpricht, *Annalen*, 1898, **303**, 279; Csányi, *Ber.*, 1919, **52**, 1788).

In the course of the present investigation, it was found that:

(1) Hydrogen chloride, as a condensing agent, facilitates the formation of hydroxyanthraquinones and phthaleins.

(2) Boric acid, as a condensing agent, assists the formation, not only of *o*-ketonic acids and hydroxyanthraquinones (Deichler and Weizmann, *loc. cit.*), but also that of phthaleins and fluorans.

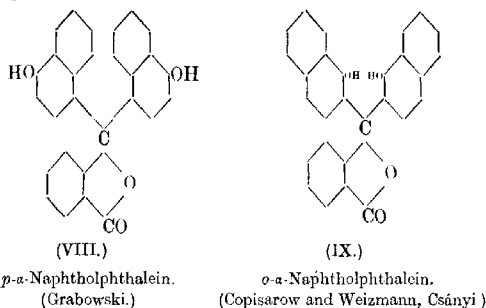
(3) Hydrogen chloride is most efficient in the presence of zinc chloride, and boric acid in the presence of concentrated sulphuric acid.

(4) The hydroxy-groups of the phthaleins are, as a rule, in the para-position, and of the fluorans in the ortho-position, with respect to the central carbon atom linking the phthaloyl with the phenolic groups. This is proved by (a) the fact that phenolphthalein is not converted into fluoran on heating above its melting point or with concentrated sulphuric and boric acids; (b) the non-formation of 4:5-dimethylfluoran, *p*-cresolphthalein, and  $\beta$ -naphtholphthalein; (c) the fact that boric acid exercises in the case of termolecular reactions (fluoran formation) the same orientating effect as in the case of bimolecular reactions (Bentley, Gardner, and Weizmann, T., 1907, **91**, 1626); this is substantiated, not only by the constitution of the fluorans, but also by the fact that the *o*-ketonic acids are an intermediate stage in the formation of fluorans from phthalic anhydride, as in the case of phthalides (Pechmann, *Ber.*, 1881, **14**, 1865; Copisarow and Weizmann, *loc. cit.*).

The apparently anomalous position of  $\alpha$ -naphtholphthalein, prepared by the hydrolysis of di-1-ethoxynaphthylphthalide, in which Copisarow and Weizmann (*loc. cit.*) assigned the hydroxy-groups to the ortho position with respect to the central carbon atom, on the ground that *o*-1-ethoxynaphthoylbenzoic acid can be regarded as an intermediate stage between phthalyl chloride and di-1-ethoxynaphthylphthalide, and also owing to the transformation of this  $\alpha$ -naphtholphthalein into  $\alpha$ -naphthasfluoran, can now be easily explained.

Grabowski (*Ber.*, 1871, **4**, 661), and Sørensen and Palitzsch (*Biochem. Zeitsch.*, 1910, **24**, 384), have indicated the possible formation of two isomeric  $\alpha$ -naphtholphthaleins, and considering

that (a) Grabowski's  $\alpha$ -naphtholphthalein cannot be converted into  $\alpha$ -naphthafuran, thus differing from Copisarow and Weizmann's  $o$ - $\alpha$ -naphtholphthalein, and (b) the  $\alpha$ -naphtholphthalein isolated by Csányi (*loc. cit.*) is identical with that of Copisarow and Weizmann (a sample preserved from 1915 and recrystallised twice from alcohol melted at 234—235°), there is no room for doubt that the following constitutions must be assigned to the two existing  $\alpha$ -naphtholphthaleins:



(5) Zinc chloride, as a condensing agent, is found to be superior to both concentrated sulphuric acid and stannic chloride, being more efficient than the former and more economical than the latter.

It was found that the alkali salts of the phthaleins, like those of phenols, are oxidised on prolonged keeping, especially on exposure to light or a current of air, giving dark, complex substances. The alkaline earth salts (barium, calcium, etc.) are less readily oxidised.

## EXPERIMENTAL.

### Zinc Chloride.

It was found that zinc chloride, prepared by evaporating to dryness a faintly acid solution of this salt, is a more efficient condensing agent than finely powdered fused sticks of zinc chloride. This superior quality is to be attributed to the fineness of division and presence of small quantities of hydrogen chloride rather than to the possible hydration of the unfused zinc chloride (compare aluminium chloride, Biltz, *Ber.*, 1893, **26**, 1960; Meyer, *Ber.*, 1896, **29**, 847), as the addition of small quantities of water to the fused zinc chloride not only does not add to, but actually diminishes, its efficiency.

*Phenolphthalein (III).*

*Preparation by means of Concentrated Sulphuric Acid.*—The condensation of phthalic anhydride with phenol in the presence of concentrated sulphuric acid was effected under the conditions given by Baeyer (*Annalen*, 1880, **202**, 69). It was found, however, that by employing an improved method of isolation and purification, the product contains about 5 per cent. of hydroxyanthraquinones. Baeyer's method of purification, consisting in pouring the decolorised alcoholic solution of the product into water, is thus ineffective. A more satisfactory method was found to be as follows.

The crude phenolphthalein, having been dissolved in aqueous sodium hydroxide and reprecipitated with hydrochloric acid, is dissolved in five times its weight of 65--70 per cent. methyl alcohol. The alcoholic solution is decolorised by boiling with animal charcoal and concentrated until solid begins to separate. On cooling and filtering, the first crop of phenolphthalein (yellow to white) is obtained; a second crop of this product is isolated on concentrating the filtrate. On further distillation, an orange-red, viscid oil separates, which, on keeping, solidifies to a brown, crystalline mass consisting of the two isomeric hydroxyanthraquinones and some phenolphthalein. The first two crops of phenolphthalein, when recrystallised from dilute alcohol, furnish snow-white crystals melting at 253°. This method of purification gives, not only phenolphthalein free from hydroxyanthraquinones, but also appears to be less wasteful than that of Baeyer, as more than 90 per cent. of the solvent is recovered. The separation of the two isomeric hydroxyanthraquinones from one another was effected according to Baeyer and Caro's method (*Ber.*, 1874, **7**, 969). The phenolphthalein accompanying the hydroxyanthraquinones is isolated by fractional crystallisation. The yield of pure phenolphthalein obtained by this method is 26 per cent. of that theoretically possible. The yield of fluoran (IV) (Baeyer, *Annalen*, 1882, **212**, 347) does not exceed 0.5 per cent.

*Preparation by means of Concentrated Sulphuric and Boric Acids.*—A mixture of 60 grams (1 mol.) of finely powdered phthalic anhydride, 80 grams (2 mols.) of phenol, 16 grams of concentrated sulphuric acid, and 8 grams of powdered boric acid was heated at 125–130° for eight hours. The product was poured into water, the mixture boiled to expel phenol, filtered white hot, and the brown residue washed with hot water. The residue was extracted several times with a 3 per cent. solution of sodium hydroxide, the extract cooled, and acidified with hydrochloric acid. The pre-

cipitate, which contained phenolphthalein and the hydroxyanthraquinones, was purified as in the previous experiment. The residue, insoluble in sodium hydroxide, crystallised from alcohol in white, rhombic crystals melting at 173–175°, and consisted of fluoran. The yield of pure phenolphthalein was 31 per cent., that of fluoran 8 per cent., and that of the hydroxyanthraquinones about 5 per cent. of the theoretical. No advantage was gained by employing boric anhydride instead of boric acid. The latter in the absence of concentrated sulphuric acid is ineffective as a condensing agent under the conditions employed.

*Preparation by means of Zinc Chloride.*—The conditions of condensation were those described by Perkin and Kipping ("Organic Chemistry," 1911, 654), the mixture being mechanically stirred. The method of purification of the products was identical with that already described. The yield of pure phenolphthalein was 47 per cent., and that of the two hydroxyanthraquinones 6 per cent., of the theoretical. The yield of fluoran was negligible. When powdered fused zinc chloride was employed, instead of zinc chloride prepared by the method described above, the yield of the products was lowered.

*Preparation by means of Hydrogen Chloride.*—From analogy to the formation of esters, it was considered possible that hydrogen chloride might serve as a condensing agent for the production of phthaleins. Investigation showed that whilst hydrogen chloride by itself is not sufficiently effective, taken in conjunction with zinc chloride, a marked improvement in the yield of phenolphthalein, and especially of the hydroxyanthraquinones, was observed. The following table shows the results of condensation by means of dry hydrogen chloride.

Experi- ment.	Phthalic anhydride. Gram- mols.	Phenol. Gram- mols.	Period of heating, in hours.	Period of passing a current of hydrogen chloride, in hours.	Yield, per cent.	Colour.
1	1	2	6.0	0.5	0.2	greyish- brown
2	1	2	6.0	6.0	0.9	dark brown
3	1	4	6.0	6.0	0.8	"
4	1	2	24.0	24.0	1.7	"

These reactions were carried out at 120–125°, the method of isolation and purification of the products being the same as in the experiments already described. The ratio of phenolphthalein to the hydroxyanthraquinones was found to be approximately 1 to 1. No fluoran was found. When the temperature was raised to 170°, the proportion of the hydroxyanthraquinones and tarry matter was increased. The results indicate that (1) the yield of product

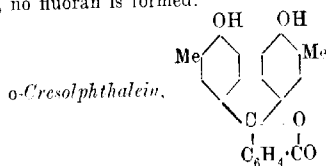
increases with the period of heating in a current of hydrogen chloride, and (2) the ratio of phenol to phthalic anhydride does not influence the yield.

These observations show a distinct difference between phthaleins and esters as regards the mechanism of their formation.

*Preparation by means of Zinc Chloride and Hydrogen Chloride.*

—A current of dry hydrogen chloride was passed through a mixture of 60 grams of finely powdered phthalic anhydride, 70 grams of zinc chloride, and 80 grams of phenol at 120—125° for half an hour, the mixture being then heated for six hours at 120—125°. The product was poured into water, which was boiled to expel phenol. The mixture was then filtered hot, washed with hot water, and the yellowish-brown residue extracted several times with a warm 4—5 per cent. solution of sodium hydroxide. The deep red alkaline solution was cooled and acidified with hydrochloric acid, and the precipitate collected, pressed, and dried. The quantity of material insoluble in alkali did not exceed 0.5 per cent. The dried precipitate was purified by decolorising with animal charcoal and fractional crystallisation from 65 per cent. methyl alcohol, as described in previous experiments. On concentrating the filtrate after the isolation of two crops of phenolphthalein, a brownish-red, viscid oil separated, which solidified on keeping. This contained hydroxyanthraquinones and phenolphthalein, the latter being about 33 per cent. of the total. The yield of pure phenolphthalein from the two crops was 52 per cent., and that of the hydroxyanthraquinones 21 per cent., the total yield of phenolphthalein being 59 per cent. of the theoretical; the 7 per cent. of phenolphthalein present in the oily residue was isolated only by a lengthy process of separation from the two hydroxyanthraquinones and fractional crystallisation, as already described. This fraction of phenolphthalein may therefore be disregarded in calculating the efficiency of this method of preparation. In subsequent experiments, the employment of hydrogen chloride was omitted.

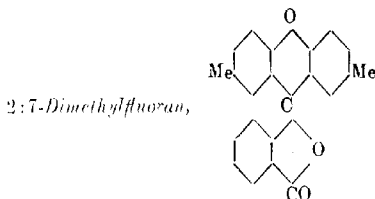
When pure phenolphthalein is heated (a) above its melting point or (b) with concentrated sulphuric and boric acids at 125—130° for eight hours, no fluoran is formed.



Baeyer (*Annalen*, 1880, **202**, 153) describes the employment of concentrated sulphuric acid and stannic chloride in the condensa-

tion of phthalic anhydride with *o*-cresol, but no indication is given either of the by-products formed or of the efficiency of each condensing agent. When phthalic anhydride was condensed with *o*-cresol in the presence of concentrated sulphuric acid under the conditions given by Baeyer, the yield was poor. A distinct improvement in yield, although this was still low, was achieved by using a mixture of concentrated sulphuric and boric acids. No 4:5-dimethylfluoran could be detected.

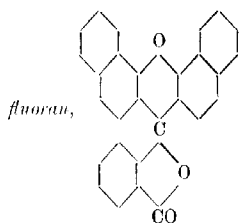
*Preparation by means of Zinc Chloride.*—Fifteen grams of phthalic anhydride and 25 grams of zinc chloride were finely powdered, 25 grams of *o*-cresol added, and the mixture was heated at 125° for eight hours. The product was worked up as in the previous experiments. On fractionally crystallising the crude precipitate from dilute alcohol, 16 grams (46 per cent. of the theoretical yield) of *o*-cresolphthalein were obtained in yellowish-white crystals melting at 216°. The last crop, fractionated by crystallising from acetic acid, was found to consist of 1-hydroxy-2-methylanthraquinone, melting at 184—185° (Bentley, Gardner, and Weizmann, T., 1907, **91**, 1634), 3-hydroxy-2-methylanthraquinone, melting at 262° (Baeyer, *Annalen*, 1880, **202**, 165), and a small quantity of *o*-cresolphthalein. No 2-hydroxy-1-methylanthraquinone could be detected. The combined yield of the two anthraquinones was about 4 per cent. of the theoretical.



The condensation of phthalic anhydride with *p*-cresol in the presence of zinc chloride was carried out in a manner similar to that employed in the case of *o*-cresol. The product, freed from *p*-cresol, phthalic acid, and zinc chloride, was extracted several times with dilute sodium hydroxide solution, and the dried residue decolorised with animal charcoal and crystallised from chloroform. It separated in yellowish-white crystals melting at 246°, and was identified as 2:7-dimethylfluoran (Baeyer, *Annalen*, 1882, **212**, 340). The brownish-red alkaline extract was acidified with hydrochloric acid, and the precipitate crystallised from glacial acetic acid in brownish-yellow needles melting at 169—170°, which were identified as 4-hydroxy-1-methylanthraquinone (Birukoff, *Ber.*,

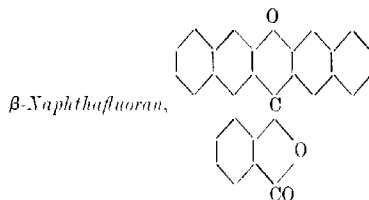
1887, **20**, 2069). The yield of 2:7-dimethylfluoran was 26 per cent., and that of 4-hydroxy-1-methylanthraquinone 2.5 per cent., of the theoretical. No trace of *p*-cresolphthalein could be detected.

*p*- $\alpha$ - and *o*- $\alpha$ -Naphtholphthaleins (VIII and IX) and  $\alpha$ -Naphtha-



*Preparation by means of Zinc Chloride.*—The condensation of phthalic anhydride with  $\alpha$ -naphthol in the presence of zinc chloride results in the formation of *o*- and *p*- $\alpha$ -naphtholphthaleins,  $\alpha$ -naphthfluoran, and small quantities of  $\alpha$ -hydroxynaphthacenequinone. Five grams of phthalic anhydride, 10 grams of  $\alpha$ -naphthol, and 15 grams of zinc chloride were finely powdered, thoroughly mixed, and heated in a flask immersed in an oil-bath at 100° for three hours. The product was extracted several times with boiling water, and then with a dilute solution of sodium hydroxide. The insoluble residue separated from benzene in small, white crystals melting at 300°, and was identified as  $\alpha$ -naphthfluoran (Grabowski, *Ber.*, 1871, **4**, 661; Meyer, *Ber.*, 1893, **26**, 207; Deichler and Weizmann, *Ber.*, 1903, **36**, 548). The deep bluish-green, alkaline extract was fractionally precipitated with hydrochloric acid and carbon dioxide according to Werner's method (T., 1918, **113**, 20). The dried precipitate was extracted with benzene, from which, on keeping, brownish-yellow crystals melting at 209° separated. This substance was identified as *p*- $\alpha$ -naphtholphthalein (Grabowski, *Ber.*, 1871, **4**, 725; 1873, **6**, 1065). It gives a deep blue coloration with alkalis, and is not converted into  $\alpha$ -naphthfluoran on heating above its melting point or with concentrated sulphuric and boric acids. On keeping the benzene mother liquors, a small quantity (about 1 per cent.) of  $\alpha$ -hydroxynaphthacenequinone (Deichler and Weizmann, *loc. cit.*; D.R.-P. 134985) was isolated in orange-red needles melting at 303°. The residue left after extracting the precipitate with benzene dissolved in ethyl alcohol, from which it separated in pinkish-yellow, prismatic needles melting at 234–235°. This substance was identified as *o*- $\alpha$ -naphtholphthalein (Copisarow and Weizmann, *loc. cit.*;

Csányi, *loc. cit.*). It gives a deep green coloration (probably due to the *o*-quinonoid structure) with alkalis, and is converted into  $\alpha$ -naphthafluoran on heating above its melting point or with concentrated sulphuric and boric acids. In this condensation, the yield of crude  $\alpha$ -naphtholphthalein (dried precipitate) was 45 per cent., whilst that of  $\alpha$ -naphthafluoran was 20 per cent., of the theoretical. The proportion of *p*- $\alpha$ - to *o*- $\alpha$ -naphtholphthalein is about 4 to 1. When the period of heating was reduced from three hours to one, the yield of crude  $\alpha$ -naphtholphthalein was increased to 50 per cent., and that of  $\alpha$ -naphthafluoran reduced to 17.3 per cent. The best yield was obtained by heating an intimate mixture of phthalic anhydride,  $\alpha$ -naphthol, and zinc chloride in a shallow basin in an air-oven at 100° for half an hour. The yield of  $\alpha$ -naphtholphthalein reached 59.3 per cent., and that of  $\alpha$ -naphthafluoran 30 per cent., of the theoretical. Sørensen and Palitzsch (*loc. cit.*) obtained a 20.7 per cent. yield of  $\alpha$ -naphtholphthalein by heating phthalyl chloride with  $\alpha$ -naphthol, whilst Werner (*loc. cit.*), carrying out the condensation of phthalic anhydride with  $\alpha$ -naphthol in the presence of concentrated sulphuric acid, found the yield to be 22.4 per cent. of the theoretical, the yield of  $\alpha$ -naphthafluoran being very small.



A mixture of 14.8 grams of phthalic anhydride, 30 grams of zinc chloride, and 28.8 grams of  $\beta$ -naphthol was heated for four hours at 100°. The product was extracted several times with boiling water and then with a hot dilute solution of sodium hydroxide. On acidifying the brownish-red, alkaline extract, a brown precipitate was obtained, which, owing to its minute quantity, could not be investigated. From analogy to other condensations, this precipitate was probably the corresponding quinone. The residue insoluble in alkalis, after being crystallised from acetic acid, melted at 293°, and was identified as  $\beta$ -naphthafluoran (Meyer, *Ber.*, 1891, **24**, 1414; 1893, **26**, 206). The yield was 12.5 per cent. of the theoretical, as compared with 7 per cent. obtained by Meyer.

The straight-line configuration for  $\beta$ -naphthafluoran may be accepted as the more probable one, for reasons similar to those



advanced in the case of phthaloyl- and diphtaloyl-carbazoles (Copisarow and Weizmann, *loc. cit.*).

The formation by  $\alpha$ -naphthol of phthaleins which give intensely coloured sensitive alkaline salts, and the failure of  $\beta$ -naphthol to form a phthalein, may be used as a colour reaction for identifying small quantities of  $\alpha$ -naphthol in  $\beta$ -naphthol.

The author wishes to express his thanks to Messrs. G. Greenwood and J. J. Sampey for assistance with the cresol condensations.

The cost of this research was partly covered by a grant from the Research Committee of the Chemical Society, for which the author desires to express his thanks.

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## XXVII.—*Certain Binary and Ternary Mixtures of Liquids having Constant Boiling Points.*

By WILLIAM RINGROSE GELSTON ATKINS.

IN the course of the distillation of commercial solvents for an industrial process, it was found necessary to study the possible mixtures of constant minimum boiling point afforded by the constituents. On examining the tables given by Young ("Fractional Distillation," pp. 67—69), and in subsequent literature, it was noticed that a number of combinations, which from their physical properties might be expected to furnish such mixtures, had not been investigated or had been examined only in a cursory manner. This work was accordingly undertaken, and the following systems were studied. The boiling points of the binary mixtures are shown under *AB*, of the ternary under *ABC*. A blank denotes that no mixture of constant boiling point is formed. Pressures are given in mm. of mercury, corrected to 0° under *P*.

At this stage, however, a copy of Lecat's exhaustive examination of such mixtures came into my hands, the work having been completed and published in Brussels in April, 1918, during the German occupation (Maurice Lecat, "La Tension de Vapeur des Mélanges de Liquides, L'Azéotropisme." Bruxelles: H. Lamertin. pp. 319).

It was found that all the binary mixtures given in this

## LIQUIDS HAVING CONSTANT BOILING POINTS. 219

A.	B.	C.	AB.	ABC.	P.
Acetone.	Carbon tetra- chloride.	Water.	55.9°	—	763
Methyl ethyl ketone.	Carbon tetra- chloride.	„	73.8	65.7°	760
„ „ „	<i>tert.</i> -Butyl alcohol.	„	79.0	—	762
„ „ „	<i>iso</i> Propyl alcohol.	„	77.3	—	759
„ „ „	<i>n</i> Propyl alcohol.	„	—	—	—
„ „ „	Ethyl alcohol.	Ethyl acetate.	*	—	—
Methyl alcohol †	Carbon disulphide.	Water.	37.1	—	751
Carbon tetra- chloride.	<i>tert.</i> -Butyl alcohol.	„	71.0	64.7	768

\* Already known.

† The addition of a little methyl alcohol to carbon tetrachloride will reveal the presence of carbon disulphide, present as an impurity, by the formation of the mixture boiling at 37.1°.

list had been studied, save *n*-propyl alcohol and methyl ethyl ketone. For all these, Lecat gives boiling points in good agreement with the figures shown here, save in the case of the mixture methyl ethyl ketone and *tert.*-butyl alcohol. For this, Lecat records that the binary mixture boils constantly at 77.5°, whereas the figure here given is 79.0°. This was obtained by adding to methyl ethyl ketone, boiling at 79.6°, 18 c.c. of the tertiary alcohol. Boiling began at 74.8°, and became constant for four observations at 79.0—79.05° at fifty-eight to twenty-eight drops per minute.

No attempt was made to analyse the binary mixtures of constant boiling point, since Lecat had done this.

Of the ternary mixtures, the only one examined by Lecat, so far as could be ascertained, was that containing carbon tetrachloride, *tert.*-butyl alcohol, and water, for which no details are given. This mixture and the corresponding one, with methyl ethyl ketone replacing alcohol, were therefore analysed.

To weighed quantities of the two major components, small weighed quantities of water were added, and the mixtures distilled up to the middle point between the boiling point of the ternary and the binary mixtures of constant boiling point in each case. It was assumed that all the water had passed over below this temperature, but this is not strictly accurate, as turbidity was still visible at the top of the distillation column near the side-tube. The quantity of carbon tetrachloride was then determined by measuring the volume it occupied after extraction of the distillate with water to remove the ketone and alcohol respectively. The latter were estimated by difference, but in the case of the ketone a direct estimation was also made by Messinger's method, adopting the usual precautions, and those advocated by Collischonn (*J. Soc. Chem. Ind.*, 1891, 10, 166) for acetone. The constant used was that 1 c.c. of *N*/10-iodine solution is equivalent to 0.00114 gram

of methyl ethyl ketone. The following are the compositions of the ternary mixtures of constant boiling point:

	Per cent.	Per cent.
Carbon tetrachloride.....	85.0	74.8
<i>tert.</i> -Butyl alcohol (by difference) .....	11.9	—
Methyl ethyl ketone (by difference) .....	—	22.2
" " " (Messinger) .....	—	20.1*
Water .....	3.1	3.0

\* It is probable that the extraction of the ketone from the chloride was not quite complete, although a large quantity of water was used.

In every case, the distillations were conducted with an electric hot plate suitably screened with asbestos board. The thermometers had been corrected at the Reichsanstalt in 1913. An eight-section Young evaporator still-head was used throughout, for the loan of which, for the use of the chemicals, and for his advice, I am indebted to Prof. S. Young. I wish also to acknowledge my indebtedness to the Chemical Society for a grant for the purchase of chemicals, and to Prof. H. H. Dixon for permission to carry out the work in the School of Botany.

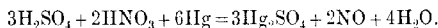
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[Received, January 29th, 1920.]

## XXVIII.—*The Estimation of Nitrogen in Nitrocellulose and Inorganic Nitrates with the Nitrometer.*

By ERNEST GEORGE BECKETT.

THE estimation of nitrogen in inorganic and organic nitrates by means of the nitrometer is based on the reaction which occurs when a solution of the nitrate in concentrated sulphuric acid is shaken with mercury. This reaction may be represented by the following equation:



The volume of nitric oxide evolved according to this equation is a measure of the quantity of nitrogen present as nitrate, and it is assumed for the purpose of calculation that the gas obtained is pure nitric oxide, and that all, and only the nitrogen present as nitrate or nitrite, has been converted into gas.

It has been known for some time that these assumptions are not correct, and hence, if the method gives trustworthy results, it can only be by a compensation of errors. Several factors have been found to exercise considerable influence on the course of the reac-

tion, and thus it is essential that the method should be standardised as far as possible. Thus Marquoyrol and Florentin (*Bull. Soc. chim.*, 1911, [iv], 9, 234) found that prolonged shaking causes a diminution of volume by reduction of the nitric oxide gas, and also a re-absorption of some of the nitrogen by the sulphuric acid. This cause of error becomes negligible if the shaking is not unduly prolonged and if the concentration of the acid is not too high.

This reaction also occurs if the nitrometer is allowed to stand after the evolution of gas has taken place, but in that case the reaction is very slow. In an experiment with gunccotton and 96.8 per cent. acid, the original volume of 109.95 c.c. became 109.80 c.c. after standing for twenty-six and a-half hours. On the other hand, the time which elapses before the mixture of mercury, sulphuric acid, and nitrocellulose has been shaken, but after the two latter substances have been introduced into the nitrometer, was found to have a marked influence on the results. This fact was discovered in the analytical laboratory of Messrs. Nobel's explosives factory at Ardeer in 1914, when the war caused a large increase in the number of nitrocelluloses to be analysed, and thus rendered almost unavoidable a certain amount of delay in carrying out the analyses.

Table I shows the influence of the time factor and of the concentration of the acid on the results at this stage of the method.

TABLE I.

*Determination of nitrogen in gunccotton with various strengths of sulphuric acid and the effect of allowing the mixture to stand before being shaken.*

Sulphuric acid. Per cent.	Interval between introducing the gunccotton and acid into the nitrometer and shaking being				
	No time.	$\frac{1}{2}$ hour.	$\frac{1}{2}$ hour.	1 hour.	17-20 hours.
99.87	12.63	—	—	11.76	—
	12.50	—	—	11.82	—
96.80	12.94	—	—	12.74	10.14
	12.945	—	—	12.68	10.28
	12.93	—	—	—	10.71
	12.96	—	—	—	—
94.0	12.975	13.065	—	13.04	11.90
92.5	12.73	13.04	13.035	13.015	12.69
	12.57	—	—	—	—

The influence of the same factors on the estimation of nitric acid is given in table II. The results given in this table with 93.3 per cent. acid were obtained with pure sodium nitrate, and those with

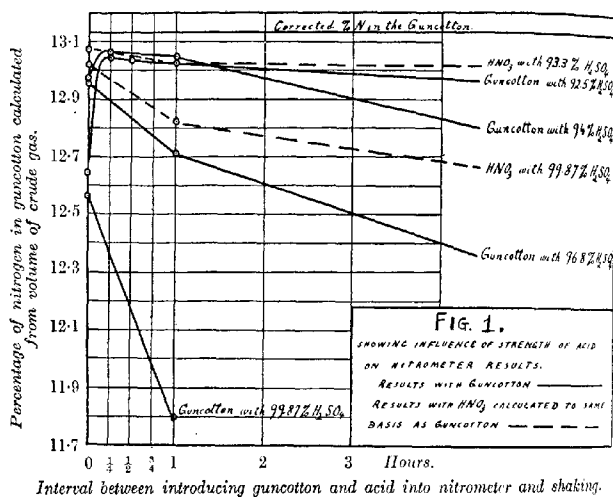
the more concentrated acid with a mixture of nitric and sulphuric acids.

TABLE II.

*Determination of nitrogen in nitric acid with various strengths of sulphuric acid and the effect of allowing the mixture to stand in the nitrometer before being shaken.*

Sulphuric acid. Per cent.	Interval between introducing the mixture into the nitrometer and shaking being		
	No time.	1 hour.	17 hours.
99.87	2.081	2.058	1.948
	2.098	—	—
93.3	16.38	16.31	16.298
	16.38	16.32	—

The results of both tables are shown graphically in Fig. 1. It will be noticed that the effect of time and concentration of acid



Interval between introducing guncotton and acid into nitrometer and shaking.

was much less in the absence of organic matter, but the influence of allowing the mixture to remain, even with 93.3 per cent. acid, is quite noticeable, and that with the stronger acid is quite marked.

Marquerol and Florentin found that the highest figures were obtained with 94 per cent. acid, but this result was not confirmed by experiments (not published) carried out by chemists in explosives works. It was generally found that 96—97 per cent. acid

gave the highest results, and thus it came about that this strength of acid is that most generally used for nitrometer work.

Neither Marquerol and Florentin nor the other chemists who investigated the question were apparently aware of the importance of the time which elapses between the introduction of the guncotton into the nitrometer and the shaking, and the discrepancies in the results may be accounted for by this.

Table I shows that the highest figures were obtained with the weaker acids, but only if a sufficient interval was allowed to elapse before shaking. If the nitrometer was shaken immediately after the guncotton was introduced, higher results were obtained with 96.8 per cent. acid than with 92.5 per cent. acid.

It is clear from these results that it is preferable to work with a weaker acid, as the results are less influenced by the time factor than they are with the stronger acid; but the most important question is to determine which results represent most closely the true nitrogen content.

Marqueyrol and Florentin, by comparing the nitrometer method with Schlösing's method, found that the former gave correct results, but it is unsafe to determine the trustworthiness of one method by comparison with another equally unproven method.

In a previous communication (*J. Soc. Chem. Ind.*, 1914, **33**, 628), the author attacked the problem in another way, and found that with guncotton and 96 per cent. acid the various errors balance one another, and that therefore the results were correct. This statement was supported by the analysis of the gas and the estimation of the nitrogen in the sulphuric acid residues by Kjeldahl's method.

It has been found since that Kjeldahl's method in this case does not show all the nitrogen—that some of the nitrogen in the residual sulphuric acid is not converted into ammonia on heating, but is given off in the form of nitrogen or nitrous oxide.

As the conclusion previously drawn must have been wrong, owing to a part of the nitrogen having escaped detection, it was decided to repeat the work on a more elaborate scale, and, so far as possible, to test every method of analysis employed with the view of discovering any source of loss.

This research deals principally with the estimation of nitrogen in nitrocelluloses, and the great difficulty was the determination of the true nitrogen content. There is no method known of ascertaining this simply and accurately. The method adopted was the same as that used in the previous investigation, namely, (1) the analysis and measurement of the gas evolved; (2) the analysis of the sulphuric acid residues. As the nitrometer estimation is carried

out in a closed glass vessel sealed by mercury, the nitrogen entering in the form of nitrocelluloses must, after the experiment, be either in the gas or in the acid, as it may be taken for granted that it cannot be absorbed in any quantity by the mercury. Besides the nitrogen introduced into the nitrometer as nitrocellulose, a small quantity enters in the form of dissolved gaseous nitrogen in the sulphuric acid. If, then, the gas is accurately analysed and measured, and all the nitrogen in the sulphuric acid residue correctly estimated, the quantity of nitrogen in the nitrometer is correctly known, and by subtracting the nitrogen introduced by the sulphuric acid, the actual quantity of nitrogen in the nitrocellulose can be calculated. This method of procedure has the advantage that the results show to what the discrepancies in the estimation by the nitrometer are due.

In this paper, the methods adopted for the analysis of the gas and the residual acid are described in Part I, and the actual experimental figures obtained are given and discussed in Part II.

## PART I.

### *Methods of Analysis.*

*Analysis and Measurement of the Gas.*—The gas was transferred from the nitrometer to a gas-analysing apparatus similar in principle to that recommended by Bone and Wheeler, but specially designed for the particular requirements of the case. The gas may contain, besides a large quantity of nitric oxide, small quantities of sulphur dioxide, carbon dioxide, nitrous oxide, nitrogen, and carbon monoxide. The analysis was carried out in the following order:

- (1) Absorption of sulphur dioxide and carbon dioxide.
- (2) Absorption of nitric oxide.
- (3) Absorption of carbon monoxide.

As the gas is evolved in the dry state in the nitrometer, it was measured dry. Great difficulty was experienced in attempting to do this at first, but by washing the measuring vessel before use with 75 per cent. sulphuric acid and leaving one or two drops of it in the vessel, the results became more satisfactory. A more concentrated sulphuric acid was not used, as nitric oxide reacts with concentrated sulphuric acid and mercury, and a weaker acid could not be used, as the vapour tension becomes too high. The vapour pressure of 75 per cent. sulphuric acid being about 0.7 mm. at the ordinary temperature, the true dry volume of the gas was taken as being 999/1000 of that measured. As the carbon dioxide and sulphur dioxide were absorbed by dry sodium hydroxide, the volume

was also measured dry after these gases had been eliminated. After absorption of the nitric oxide by ferrous chloride solution, the residual gas was measured wet, and as the volumes of gas dealt with at this stage of the analysis were comparatively small, no appreciable error was incurred in neglecting the vapour tension. In order to avoid a constant drying of the apparatus, one part was used exclusively for measuring the dry gas and another part only for the latter portion of the analysis. The gas was first transferred from the nitrometer into a gas-measuring vessel, which was immersed in water, kept stirred by a stream of air being bubbled through it, and measured dry after having been brought to atmospheric pressure.

*Estimation of the Carbon Dioxide and Sulphur Dioxide.*—Owing to the possibility of carbon dioxide and sulphur dioxide being absorbed by the reagents used for eliminating the nitric oxide, these were estimated first. Alkali hydroxides are stated to react with nitric oxide, and this was found to be, indeed, the case with solid potassium hydroxide. Solid sodium hydroxide, however, was found to have no influence, as the following figures show.

TABLE III.

*Showing the action of nitric oxide on potassium hydroxide.*

	Volume of gas at N.T.P. in c.c.	Difference in c.c.
Original volume.....	110.36	—
After one hour over KOH .....	109.22	1.14
After another hour over KOH the latter having been moistened .....	109.08	0.14
After another hour .....	108.59	0.49
" " .....	107.90	0.69
" " .....	107.22	0.68

The large diminution in volume which occurred at first was due to the presence of carbon dioxide and sulphur dioxide in the gas. The gas was then allowed to act on a stick of solid sodium hydroxide.

TABLE IV.

*Showing the action of nitric oxide on sodium hydroxide.*

	Volume of gas at N.T.P. in c.c.	Difference in c.c.
Original volume.....	107.11	—
After one hour over NaOH .....	107.09	0.02
After another hour over NaOH which had been slightly moistened .....	107.16	-0.07
After another hour and a half .....	107.13	0.03
After two hours over a stick of calcium chloride .....	107.08	0.05



In the actual analysis, the gas was allowed to remain for two to three hours in contact with the stick of sodium hydroxide. The latter was tested on several occasions for nitrites and nitrates by Devarda's method, in order to ascertain if any nitrogen was abstracted from the gas by this treatment, but no appreciable quantity could be found.

*Estimation of the Nitric Oxide.*—The gas, after absorption of the carbon dioxide and sulphur dioxide, consisted mainly of nitric oxide, and contained also small quantities of carbon monoxide, nitrogen, and nitrous oxide. The latter gas, owing to its great solubility in most solutions, gave much trouble, but a concentrated solution of ferrous chloride seemed to be specially suited for separating nitrous oxide from nitric oxide, as the solubility of the former gas in it was found to be about 16 per cent. at the ordinary temperature. Altogether, 9 c.c. of ferrous chloride solution were generally used for absorbing the nitric oxide, and this solution could have absorbed 1.4 c.c. of nitrous oxide. Under the conditions of the experiment, however, it was found by a trial with a synthetic mixture that not more than 0.34 c.c. was absorbed during the analysis of a mixture containing 9 c.c. of nitrous oxide and 109 c.c. of nitric oxide. When the quantity of nitrous oxide was much smaller, as was usually the case, the loss must have been much less.

In the actual analysis, the gas was treated with 7 c.c. of concentrated ferrous chloride solution until no further diminution of volume occurred. It was then treated with 0.5 to 0.75 c.c. of the same solution for one to two hours at ordinary atmospheric pressure. Very little diminution occurred as a rule during this last treatment. The gas was then immediately measured. Washing with water is not permissible, as the solubility of nitrous oxide at the ordinary temperature is about 80 per cent. by volume. It was found that even with the small quantities of gas usually dealt with at this stage of the analysis, treatment with 2 c.c. of water caused a loss of 0.3 c.c., although the gas contained a large proportion of nitrogen and its volume was only about 1 c.c.

*Estimation of Carbon Monoxide.*—The solubility of nitrous oxide in ammoniacal cuprous chloride was found to be about 30 per cent. by volume, that is, twice that in ferrous chloride. Moreover, treatment with ammoniacal cuprous chloride has always to be followed by a treatment with water or dilute acid to absorb the ammonia left in the gas. This double treatment caused such an appreciable loss of nitrous oxide that the use of this absorbent for carbon monoxide had to be avoided. Acid cuprous chloride was found to be no better.

An attempt was made to analyse the mixture by keeping the gas over a heated mixture of copper oxide and copper. The carbon monoxide would be oxidised to carbon dioxide, and the nitrous oxide reduced by the copper to nitrogen. This method was found to work quite well if the gas was kept for half an hour in contact with the mixture at  $250^{\circ}$ . One treatment was found to be sufficient when the gas was poor in carbon monoxide, but when the latter was present to the extent of 50 per cent. or more, two treatments were necessary.

The copper was prepared by precipitation from a solution of copper chloride with a rod of pure zinc. Copper sulphate could not be used for this purpose, as the product then contains small quantities of copper sulphide. The copper oxide was first prepared by igniting copper nitrate, but it was found that the ordinary copper oxide, as used for combustions, made by igniting copper wire, was just as suitable.

A mixture of about equal parts of these two substances was placed in a glass bulb having a little more than twice the volume of the gas to be analysed, and the bulb connected to the gas-measuring apparatus by a glass capillary tube and an indiarubber tube connexion. Before each experiment, a small piece of fresh filter paper was inserted in the capillary tube to absorb any liquid which it was difficult otherwise to prevent from being drawn into the bulb. The bulb and contents were then heated in an oil-bath to  $250$ – $280^{\circ}$  and exhausted. The gas to be analysed was admitted, heated for an hour, and pumped out again. The volume was then measured, the carbon dioxide absorbed, and the volume measured again. The diminution represented the volume of carbon monoxide. As the proportion of the latter gas was small, by adopting the procedure described, incomplete exhaustion of the bulb before the treatment had no effect on the results, and even if a trace of the gas had been left in the bulb after treatment, the accuracy of the analysis was not appreciably impaired.

No attempt was made to ascertain the proportion of nitrous oxide to nitrogen in the nitrometer gas. They were both classed together, as they contain the same quantity of nitrogen per c.c.

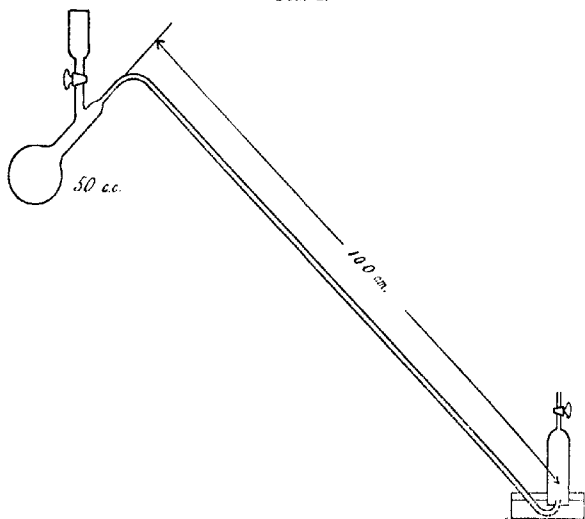
#### *Estimation of the Nitrogen in the Sulphuric Acid Residues.*

*Estimation of the Gases Evolved on Heating.*—A flask of the shape shown in Fig. 2 was filled with mercury, care being taken that no air was left adhering to the sides of the vessel. It was then inverted, with the end of the long tube dipping in a trough of mercury. By this means, a Torricellian vacuum was produced

in the vessel, which contained no appreciable quantities of permanent gas.

The sulphuric acid residue was transferred from the nitrometer to the funnel, and allowed to be drawn into the vessel, care being taken that no air was sucked in with it. The nitrometer was washed with two quantities of 5 c.c. of sulphuric acid, which were also transferred to the flask in the same way. The flask was gently heated, as in a Kjeldahl estimation, and the sulphur dioxide produced by the action of the mercury which had been left in the stopper of the apparatus and had been sucked in, together with

FIG. 2.



the sulphuric acid, swept out all the other gases in a comparatively short time. The gases were collected over 20 c.c. of a 30 per cent. solution of potassium hydroxide, and consisted in the case of gun-cotton mainly of carbon monoxide with a little nitrogen and nitrous oxide. The acid from an analysis of an inorganic substance gave only nitrogen and nitrous oxide. It is curious that nitric oxide was never found in these gases in appreciable quantities, although the sulphuric acid must have been saturated with the gas when it was in the nitrometer. The mercury dissolved in the sulphuric acid is in the form of mercurous sulphate in the nitrometer, but after the acid has been heated, the mercurous sulphate

is converted into mercuric sulphate. No doubt the nitric oxide is reduced at the higher temperature by the mercurous sulphate to nitrogen or nitrous oxide.

After the evolution of gas had almost ceased, which occurred when the drop of mercury had dissolved, the sulphuric acid was heated to boiling until the liquid appeared transparent, but not necessarily colourless. Experiment showed that heating until colourless, and heating for several hours after the acid had become colourless and after the addition of potassium sulphate, had no effect on the amount of ammonia formed in the sulphuric acid.

The gas collected over the potassium hydroxide, which in the case of nitrocellulose usually amounted to 2 to 3 c.c., was transferred to the wet gas analysis apparatus, and the carbon monoxide removed by heating over copper and copper oxide and treatment with sodium hydroxide. In this case, where the quantity of carbon monoxide was very much greater than that of the nitrogen gases, the actual residue of nitrogen was measured, and not the diminution in volume on treatment with potassium hydroxide, as described above.

Experiments were carried out in order to ascertain whether the 20 c.c. of potassium hydroxide dissolved an appreciable quantity of nitrous oxide, which would thus escape detection. A concentrated sulphuric acid was prepared containing a known volume of dissolved nitrous oxide in solution. A weighed quantity of this acid was subjected to the same treatment as the sulphuric acid residues from the nitrometer estimations, and the volume of gas obtained was only 0.11 c.c. short of that which the acid contained. This experiment represents an extreme case, as the quantity of the gas was greater than that usually found, and it consisted of pure nitrous oxide, whereas in the actual analysis of nitrocellulose acid, the proportion of nitrous oxide in the gas must have been less than 25 per cent.

The potassium hydroxide after an experiment with nitrocellulose was examined for nitrates and nitrites by Devarda's method, but none could be found. Blank experiments were always carried out with the same quantities of the same sulphuric acid as used in the actual analysis, and the results obtained in these really represent the quantity of gas dissolved in the sulphuric acid. In the blank experiments, however, the gas contained also a small quantity of oxygen, which had to be removed with alkaline pyrogallol solution.

*Estimation of Ammonia formed in the Acid.*—The sulphuric acid after it had been boiled until transparent was transferred to a round-bottomed litre flask, and after adding an excess of sodium

hydroxide and sufficient sodium sulphide to convert all the mercury present into sulphide, the ammonia was distilled off into a known quantity of  $N/100$ -acid. The acid was then titrated with  $N/100$ -sodium hydroxide.

Blank determinations were always carried out with the same quantities of the same sulphuric acid, sodium hydroxide, sodium sulphide, and water as in the actual analysis.

Many attempts were made here also to ascertain if any loss of nitrogen occurred.

The ammonia distillation was carried out with the addition of Devarda's alloy and other reducing agents in a variety of ways without increasing the result.

The distillation of ammonia was also carried out under diminished pressure, and the evolved gases were collected, but the quantity of gas so obtained, namely, 0.29 c.c., was not much greater than that given off in a blank determination, namely, 0.20 c.c.

The addition of sodium sulphide was found to be essential.

## PART II.

### *Discussion of Results Obtained.*

The following are the details of the nitrometric method which was used for obtaining the results given in this paper. The method is similar to that used in many explosive factories.

The nitrometer was first washed out with concentrated sulphuric acid, and the cup washed with distilled water and dried.

Dried and sieved nitrocellulose (0.5—0.55 gram) was placed in a weighing bottle and heated to  $96^{\circ}$  in a steam-bath for one hour. The weighing bottle was then accurately weighed, the nitrocellulose dropped into the cup of the nitrometer, and the empty weighing bottle weighed again. Five c.c. of the sulphuric acid of specified strength were added to the cup, the nitrocellulose was stirred in the acid with a glass rod, and run into the nitrometer. The cup was then washed with successive quantities of 2.5 c.c., 2.5 c.c., and 5 c.c. of the same acid, and these were run into the nitrometer as well. The whole operation of washing the nitrocellulose into the nitrometer with the 15 c.c. of acid occupied five minutes. After the introduction of the acid and nitrocellulose, the nitrometer was allowed to stand for the specified time and then vigorously shaken for one and a-half minutes. It was allowed to stand for ten minutes, again shaken vigorously for one minute, and the gas transferred to the measuring vessel described above.

The sodium nitrate was introduced into the nitrometer cup in

TABLE V.  
Giving analyses of the various products of nitrometer determinations.

Substance used.	Sulphuric acid. Per cent.	Interval between introducing gun-cotton and acid into the nitrometer and shaking.	Sub-stance used. Grams.	Analysis of gas.			Analysis of residual acid.		N <sub>2</sub> in acid used for analysis, c.c.	Nitrogen calculated from volume of crude gas, Per cent.	Corrected nitrogen content, Per cent.	Correction to be added to percentage of nitrogen from crude gas.
				CO <sub>2</sub> and SO <sub>2</sub> , c.c.	CO, c.c.	N <sub>2</sub> and N <sub>2</sub> O, c.c.	N <sub>2</sub> and N <sub>2</sub> O evolved as gas, c.c.	NH <sub>3</sub> formed in acid as c.c. NO.				
Dupont high nitrogen gun-cotton.	96.8	None	0.51135	106.76	0.25	0.25	0.82	0.59	1.16	0.39	13.44	0.23
	96.8	None	0.50965	106.27	0.30	0.25	0.85	0.62	1.20	0.39	13.45	0.255
	96.8	None	0.54865	111.81	0.64*	0.22	0.82	0.485	1.20	0.39	13.085	0.155
Juncotton. ...	96.8	None	0.5263	107.69	0.47*	0.17	0.80	0.50	1.13	0.39	12.96	0.18
	96.8	None	0.54415	109.03	0.21	0.16	0.63	0.58	0.94	0.39	12.82	0.19
	96.8	None	0.53975	107.94	0.15	0.21	0.66	0.59	0.94	0.39	12.81	0.25
Highly soluble nitrocellulose.	96.8	None	0.55375	104.65	0.22	0.26	0.95	0.68	1.16	0.39	12.18	0.25
	96.8	None	0.55155	104.37	0.22	0.25	0.73	0.635	1.12	0.39	12.18	0.215
	96.8	None	0.4513	117.70	0.11	—	0.48	0.35	0.15	0.39	16.382	0.065
Pure sodium nitrate (Kahlbaum).	96.8	None	0.45265	118.09	0.03	—	0.50	0.40	0.08	0.39	16.382	0.077
	96.8	None	0.52525	102.23	1.10	0.23	1.49	0.72	4.75	0.62	13.115	0.615
	96.8	20 hours	0.5294	76.43	2.29	1.30	10.70	2.06	8.83	0.39	12.9	2.19
Juncotton ...	92.5	None	0.5316	105.86	0.26	0.08	0.65	—	3.28	0.30	12.57	—
	92.5	4 hours	0.5228	107.72	0.66	0.16	0.53	0.45	0.98	0.30	13.04	0.10
	96.8	17 hours	0.4509	116.37	0.20	—	0.98	0.38	0.27	0.39	16.44	0.14
Sodium nitrate	99.87	None	2.867	95.08	0.45	—	0.75	0.67	0.07	0.62	—	—
	99.87	17 hours	3.140	97.79	2.19	—	3.27	1.94	1.29	0.62	—	—
	99.87	17 hours	3.140	97.79	2.19	—	3.27	1.94	1.29	0.62	—	—

\* Other results for the determination of carbon dioxide in the gas from gun-cotton were also obtained, but they were not added to the table as the analyses were not completed. These results for a similar quantity of gas were 0.57, 0.57, 0.40, 0.59, 0.56 c.c.

the same way as the guncotton, but it was then dissolved in two portions of water of 0.5 c.c. each, which were run into the nitrometer, and the cup was washed with 96.8 per cent. sulphuric acid, as described above. In this case, the addition of the water reduced the concentration of the acid to 93.3 per cent.

The results are given in table V.

The results for the various kinds of nitrocellulose under the same conditions show that they act in the nitrometer in the same way under normal conditions with 96.8 per cent. acid; the only essential difference observed was the quantity of carbon dioxide and sulphur dioxide in the gas evolved from guncotton. This difference is not caused by any special behaviour of the guncotton itself, but by the presence of calcium carbonate, as the following figures show.

TABLE VI.

*Giving percentage of calcium carbonate in the nitrocelluloses used.*

	CaCO <sub>3</sub> Per cent.	CO <sub>2</sub> from 0.53 grain. c.c.
Dupont high nitrogen guncotton ...	0.02	0.025
Guncotton .....	0.25	0.29
Highly soluble nitrocellulose .....	0.02	0.025
Blasting soluble nitrocellulose.....	0.06	0.07

Taking the figures as a whole, it will be seen that under all the conditions examined, the results calculated from the crude gas with both inorganic and organic nitrates were too low. The best result for guncotton was obtained with 92.5 per cent. acid and an interval of fifteen minutes between the introduction of the guncotton and acid into the nitrometer and the shaking. It will also be observed that the best results are concomitant with a high degree of purity of the gas and, at the same time, a small content of nitrogen in the residues. With guncotton, the purest gas is obtained with 92.5 per cent. acid, and no interval between the introduction of the nitrocellulose and the shaking; but in this case a large amount of nitrogen is retained by the acid, due, apparently, to incomplete decomposition of the guncotton.

The table also shows that the errors in the case of inorganic nitrates are smaller than they are with nitrocelluloses; hence the standardisation of the nitrometer with pure sodium or potassium nitrate does not necessarily eliminate the errors of the determination of nitrogen in organic nitrates.

The use of the more dilute sulphuric acids is advisable, not only on account of the better results obtained, but also because they generally contain a smaller quantity of dissolved nitrogen.

Nitrogen appears to dissolve in a greater degree the more con-

centrated the acid between the limits of 90 and 100 per cent.; hence more dissolved nitrogen is usually found in the more highly concentrated acids, as the figures in table VII show. These figures have been calculated from the blank experiments mentioned on p. 229.

TABLE VII.

*Dissolved nitrogen in concentrated sulphuric acid.*

Sulphuric acid. Per cent.	Percentage of nitrogen by volume.
99.87	3.09
96.8	1.56
94.0	1.11
92.5	0.98

The nitrogen from the sulphuric acid is partly driven out during an estimation by the escaping nitric oxide, and is thus partly responsible for the content of nitrogen in the latter gas.

The separate estimation of nitrogen and nitrous oxide in the nitric oxide was not carried out in the above analyses, as these two gases contain the same quantity of nitrogen per c.c. In two cases, however, this was determined by combustion with hydrogen. The crude nitric oxide was obtained by shaking guncotton with 96 per cent. sulphuric acid, after allowing the mixture to remain in the nitrometer for about twenty-four hours. In one case this gas contained 4.6 per cent. of nitrogen and 6.8 per cent. of nitrous oxide; in the other experiment, the gas was found to contain 5.8 per cent. of nitrogen and 5.6 per cent. of nitrous oxide.

The large quantity of gas evolved on heating the residual sulphuric acid in some of the experiments described in table V was explained by the great solubility of nitrous oxide in concentrated sulphuric acid, which was found to be about 58 per cent. by volume at the ordinary temperature.

#### *Influence of the Quantity of Sulphuric Acid.*

The question of the influence of the quantity of sulphuric acid used is of importance, as many firms, especially those in America, use 50 c.c. of 94–94.5 per cent. sulphuric acid and the Lunge volumometer, instead of 15 c.c. as in the ordinary nitrometer. Apparently the larger quantity of acid is used to accelerate the decomposition, which with a smaller quantity of this strength of acid might remain incomplete unless a sufficient interval were allowed between the introduction of the guncotton and the shaking. The larger quantity of nitric oxide dissolved in the acid is com-



TABLE VIII.  
*Giving results obtained with 50 c.c. of 94 per cent. sulphuric acid.*

Substance used.	No. of expt.	Sub- stance, Gram.	Crude gas at N.T.P. c.c.	Nitrogen calculated from crude gas. Per cent.	Nitrogen in acid used for analysis c.c.	Composition of gas.	Composition of acid.	Corrected content of nitrogen cal. as c.c. NO.	Corrected nitrogen content. Per cent.
Guncotton	1	0.5253	108.09	12.86	0.71	From No. 2. NO = 106.48 c.c. SO <sub>2</sub> and CO <sub>2</sub> = 0.32 c.c. CO = 0.13 c.c. N <sub>2</sub> and N <sub>2</sub> O = 1.13 c.c.	From No. 2. N <sub>2</sub> and N <sub>2</sub> O as gas = 0.94 c.c.	110.40	13.15
	2	0.52485	108.06	12.87					
	3	0.52545	108.35	12.89			NO present as ammonia = 1.20 c.c.		
	Mean.	—	—	12.87		—	—	—	13.15
Pure sodium nitrate	4	0.4511	117.52	16.29	0.71	From No. 7. NO = 116.50 c.c.	—	—	—
	5	0.4497	116.93	16.255			—	—	—
	6	0.4459	115.87	16.245		SO <sub>2</sub> = 0.04 c.c.	—	—	—
	7	0.44975	117.23	16.29		N <sub>2</sub> and N <sub>2</sub> O = 0.69 c.c.	—	—	—
	Mean	—	—	16.27					

compensated by standardising the measuring apparatus with pure potassium nitrate. The results obtained with 50 c.c. of 94.0 per cent. acid are given in table VIII.

The results show that the ammonia formed in the residual acid is the same as with a smaller quantity of a similar acid, but that all the other sources of error are greater; hence the actual volume of gas obtained is smaller than with the ordinary nitrometer, and even standardisation with potassium or sodium nitrate does not produce results any higher or truer than those obtainable with the ordinary nitrometer.

It may be mentioned here that in the experiments with sodium nitrate, the addition of 1 c.c. of water to 50 c.c. of 94 per cent. acid produced an acid of about 93 per cent., that is, practically the same as that obtained in the other experiments with sodium nitrate, where 15 c.c. of 96.8 per cent. acid were diluted with 1 c.c. of water.

#### *Conclusion.*

The general result of the research is that the nitrometric estimation of nitrogen in nitrocelluloses invariably gives results which are too low.

It has been found that the interval of time which is allowed to elapse between the introduction of the nitrate and sulphuric acid into the nitrometer and the shaking has a great influence on the results in the case of nitrocelluloses. The effect is less in the case of inorganic nitrates.

The truest results are obtained by using 15 c.c. of 92.5—94.0 per cent. sulphuric acid, and by allowing a quarter to half an hour to elapse between the introduction of the nitrocellulose and acid into the nitrometer and the shaking. In this case, the error is about 0.7 per cent., taking the nitrogen as 100.

This research was carried out in the Research Laboratories of Nobel's Explosives Co., Ardeer, and I wish to express here my thanks to Mr. J. Rogers, O.B.E., and to Mr. W. Rintoul, O.B.E., for their kind permission to publish the results.

FALKIRK,  
STIRLINGSHIRE.

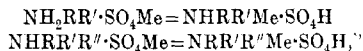
[Received, November 10th, 1919.]

### XXIX.—*The Preparation of Methylamine from Ammonium Methyl Sulphate.*

By WILLIAM SMITH DENHAM and LIONEL FREDERICK KNAPP.

WERNER (T., 1914, 105, 2762), who observed that methylamine is produced when ammonium methyl sulphate is heated, followed acidimetrically the progress of the change to temperatures up to 275°, and regards it as being represented essentially by the equation  $\text{NH}_4\cdot\text{SO}_4\text{Me}=\text{NH}_3\text{Me}\cdot\text{SO}_4\text{H}$ , although at temperatures above 240° a small quantity of ethylene is formed owing to a subsidiary reaction. He records the separation under favourable conditions of an 85.6 per cent. yield of methylamine. The methyl sulphates of the substituted ammonium bases behave similarly when heated, and the discoverer suggests that those reactions may be found of practical value for the preparation of the substituted methylammonium bases.

The results now communicated, obtained in an investigation of Werner's reaction undertaken with the object of utilising it for the preparation of methylamine, indicate that, under the conditions observed, the reaction is less simple than represented above, and that, at any temperature at which a noticeable transformation of ammonium methyl sulphate occurs, a mixture is produced containing ammonium, methylammonium, dimethylammonium, trimethylammonium, and (probably) tetramethylammonium salts, as, indeed, is implied in Werner's statement that "the further progress and limit of the isomeric transformation may be expressed by the general equations:

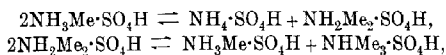


for, once some methylamine is produced, the melted mass may be considered, as pointed out by Werner, to contain methylamine methyl sulphate among other salts.

It is evident that the formation of secondary and tertiary amines need not become apparent in the acidimetric values, since, as indicated by equations given below, an interconversion of the amines may cause no alteration in the amount of free acid present. The products of the transformation were therefore separated approximately, and from these analyses it is concluded that, by heating ammonium methyl sulphate alone, about 25 to 30 per cent. of the ammonia can be converted into methylamine. When the period of heating is prolonged, the proportion of dimethylamine

and trimethylamine (taken together) in the product increases, but the absolute amount of methylamine does not alter very much.

Methylamine is produced when a mixture of the sulphate of ammonium, dimethylamine, and trimethylamine is heated, and this supports the view that in the melted mass obtained by heating ammonium methyl sulphate, a state of equilibrium is attained or approximated to in which, as expressed by the equations

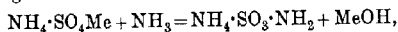


salts of methylamine and ammonium are opposed. The addition of ammonium salts to the ammonium methyl sulphate may therefore be expected to increase the yield of methylamine, an expectation which is in accordance with the fact. When one equivalent of ammonium sulphate was mixed with ammonium methyl sulphate, a distinct improvement was observed in the yield of methylamine, but the mixture does not melt very readily, and, possibly on account of the imperfect fusion, the yield was not further increased when two equivalents of ammonium sulphate were added. Of the few other ammonium salts which it appeared to be practicable to use, ammonium benzenesulphonate was chosen. With ammonium methyl sulphate, this salt forms an easily fusible mixture, from which a greatly increased yield of methylamine is obtained, whilst the proportion of dimethylamine and trimethylamine produced (taken together) is greatly diminished.

The possibility that the beneficial effect of the presence of ammonium benzenesulphonate may be related to the known methylating action of methyl benzenesulphonate was not investigated; although this possibility might account for an increased yield of methylamine, it does not explain the alteration in the relative proportions of methylamine on the one hand and dimethylamine and trimethylamine on the other if we suppose the subsequent transformations to be reversible. No further sulphonation of the benzene residue was observed, and the improved yield cannot therefore be ascribed to a partial removal in this way of free sulphuric acid, the presence of which, indeed, does not appear to be harmful and is probably necessary.

The employment of gaseous ammonia suggests itself as a means of neutralising the free acid (supposing that desirable) and of supplying at the same time an increased concentration of ammonium salts, and an improved yield of methylamine was indeed obtained when ammonia in regulated amounts was admitted to the reaction vessel, but the method is inconvenient. At the ordinary temperature, ammonia reacts with ammonium methyl sulphate

with the evolution of heat, probably owing to the occurrence of the following or some similar reaction,



and no methylamine is produced.

It is concluded that, to obtain the best yield of methylamine by means of Werner's reaction, the ammonium methyl sulphate should be heated for one hour and a-half at  $260^\circ$  or at a slightly higher temperature, when the yield of methylamine is about 27 per cent. of the theoretical yield; when a mixture of ammonium methyl sulphate with two equivalents of ammonium benzenesulphonate is heated under conditions otherwise the same, the yield of methylamine is nearly 50 per cent. of the theoretical.

#### EXPERIMENTAL.

In most of the experiments summarised in the following tables, 1/10th gram-molecule (12.9 grams) of ammonium methyl sulphate contained in a test-tube was heated in an oil-bath. Excess of sodium hydroxide was added to the aqueous solution of the product, and the liberated bases were distilled, usually under diminished pressure, into aqueous hydrochloric acid. The hydrochloric acid solution of the amines was then evaporated, at first on the water-bath under atmospheric pressure, and finally in a vacuum until the weight was constant. The dried mass was extracted twice by boiling with absolute alcohol, using 50 c.c. of alcohol for the first extraction and 25 c.c. for the second, and the residue of ammonium chloride was washed with 25 c.c. of cold alcohol. (When very large quantities of ammonium salts were present, a preliminary extraction was made with much alcohol, and the residue from the evaporation of the solution thus obtained was then extracted as above.) After removing the alcohol by distillation from the united alcoholic extracts and washings, the residual mixture of ammonium chloride and amine hydrochlorides was dried until constant in weight, and in some experiments this residue was extracted twice by boiling it with chloroform, using 50 c.c. of the solvent each time. According to Bresler (*Ann. Chim. anal.*, 1901, **6**, 28; compare Behrend, *Annalen*, 1884, **222**, 119), methylamine hydrochloride is insoluble in hot chloroform, whilst the hydrochlorides of dimethylamine and trimethylamine dissolve quite readily. When ammonium chloride alone was boiled with 50 c.c. and 25 c.c. of alcohol successively, the united extracts gave on evaporation 0.55 gram of ammonium chloride, and in the calculation of the "yield of methylamine" from the weight of the alcoholic extract, 0.55 gram has been deducted as an approximate

correction for the ammonium chloride present. The "yield" thus found is employed merely as a conventional method of comparing the results of experiments when more accurate methods of comparison are not available, for the alcoholic extract contained the hydrochlorides of dimethylamine and trimethylamine, and probably more ammonium chloride than was allowed for. The residue from the extraction with chloroform contained, besides methylamine hydrochloride, the ammonium chloride present in the alcoholic extract, and in calculating the "yield of methylamine" from the quantity of product dissolved by alcohol, but undissolved by chloroform, the same weight (0.55 gram) was first deducted. In several experiments, the proportion of methylamine in the residue from the extraction with chloroform was determined by François' method (*Compt. rend.*, 1907, **144**, 857), that is, by fixing the ammonia with yellow mercuric oxide and titrating the methylamine in the filtrate.

In each of the experiments of which the results are summarised in this table, a tube containing 20 grams of ammonium methyl sulphate was placed in an oil-bath already heated to the desired temperature and removed after thirty minutes, the contents of the tube being at the maximum temperature for periods varying between fifteen and twenty minutes. Two-fifths of the product (derived from 8 grams of ammonium methyl sulphate) were used for titration, and from the remainder the amine hydrochlorides were prepared and extracted with alcohol, as described above. Although the part of the product treated in this way was derived from only 12 grams of ammonium methyl sulphate, the same approximate correction was made for the ammonium chloride present as in the experiments in which 12.9 grams were used, since the same quantities of alcohol were employed in the extractions. Werner's results by titration after fifteen minutes' heating at nearly equal temperatures are given for comparison. The "yields of methylamine" are expressed as percentages of the theoretical yield if complete transformation occurred. The weight of methylamine hydrochloride from 12 grams of ammonium methyl sulphate would then be 6.27 grams.

Effervescence occurred in all cases, especially in 3 and 4, where the temperatures in the tubes rose above that of the bath, but both the effervescence and the evolution of heat slackened after a few minutes. The fused products from experiments 1 and 2 were slightly yellow; those from 3 and 4 were dark reddish-brown.

TABLE I.

No. of experiment.	Total duration of heating Minutes.	Period at maximum temperature.	I. Amino hydrochlorides dissolved by alcohol (grams).	II.	III. Yield of methylamine calculated from III after correction for $\text{NH}_4\text{Cl}$ .	IV. Yield of methylamine from titration.	V. "Isomeric change" at nearly equal temperatures (Werner).
1	30	16 min. at 160—165°	0.61		1.0	2.2	11.5 (160°)
2	30	18 " 200—205°	1.17		10.0	23.8	25.8 (200—205°)
3	30	22 " 255—260°	3.94		54.1	89.6	85.9 (250—260°)
4	30	22 " 274—275°	4.19		58.1	95.6	97.2 (275°)

TABLE II.

In the experiments summarised here, the period of heating was longer. 12.9 Grams of ammonium methyl sulphate were used for each experiment, the theoretical yield of methylamine hydrochloride being 6.75 grams.

The temperatures are those of the bath, initially at the ordinary temperature.

		I.	II.	III.
No. of experiment.	Duration of heating. Hours.	Temperature, etc.	Weight of amine hydrochlorides dissolved by alcohol. Grams.	Yield of methylamine calculated from II after correction for ammonium chloride. Percentage of the theoretical yield.
5	100	100°	0.69	2.1
6	7	{ 5 hours up to 168°. } { 2 hours at 160—168°. }	0.70	2.2
7	6½	{ 2 hours up to 206°. } { 4½ hours at 196—206°. }	3.24	39.9
8	6	{ 3 hours up to 255°. } { 3 hours at 230—255°. }	3.89	49.5
9	1½	{ 1 hour up to 272°. } { ½ hour at 240—272°. }	4.52	58.8

*Partial Solubility of the Amine Hydrochlorides in Chloroform.*  
—Table III shows the proportion of the alcohol-soluble product.

TABLE III.

12.9 Grams of ammonium methyl sulphate were heated in each experiment, the theoretical yield of methylammonium chloride being 6.75 grams.

No. of experiment.	Duration of heating. Mins.	I. Temperature.	II. Weight of amine hydrochlorides dissolved by alcohol. Grams.	III. Weight of amine hydrochlorides dissolved by alcohol but undissolved by chloroform. Grams.	IV. Yield of methylamine calculated from II after correction for ammonium chloride. Percentage of the theoretical yield.	V. Yield of methylamine calculated from III after correction for ammonium chloride.
10	18	230—234°	3.0	2.1	36.3	23.0
11	17	254—258°	3.74	2.44	47.3	28.0
12	16	From room temperature to 260°	3.47	2.62	43.3	30.1



found to be insoluble in chloroform. The results are confirmed by those displayed in later tables. In experiments 10 and 11, the vessels containing the ammonium methyl sulphate were placed in an oil-bath already heated to the required temperature. In experiment 12, the ammonium methyl sulphate was heated in sixteen minutes from the ordinary temperature to  $260^{\circ}$ , and then removed from the bath, when the temperature of the melted salt remained at about  $260^{\circ}$  for a minute or two, and then fell slowly.

*Nitrogen in the Still Residue.*—In experiment (10), after the volatile bases had been removed by prolonged distillation of the alkaline solution of the product obtained on heating the ammonium methyl sulphate, the residue in the distillation flask was neutralised with sulphuric acid and evaporated to dryness. The dried residue was found to contain nitrogen.

*Effect of Ammonia on the Transformation.*—In experiment (13) (table IV), a very slow current of ammonia was passed into the salt after it had been melted and heated to  $170^{\circ}$ ; in experiment (14), the flask containing the salt was heated rapidly to  $220^{\circ}$ , and then attached to a reservoir of ammonia gas under a pressure of 100 mm., in addition to the atmospheric pressure; and in experiments (15), (16), and (17), ammonia, similarly under a slightly increased pressure, was present from the beginning. If the yield of methylamine were theoretical, and if all the acid formed were neutralised by ammonia, the total weights of hydrochlorides in column III would be 12.1 grams (5.35 grams of ammonium chloride and 6.75 grams of methylamine hydrochloride).

TABLE IV.

12.9 Grams of ammonium methyl sulphate were heated in each experiment. The oil-bath and contents were heated from the ordinary temperature. The temperatures are those of the bath.

No. of experiment.	Duration of heating. Hours.	Temperature.	Weight of amine hydrochlorides. Grams.	Weight of amine hydrochlorides dissolved by alcohol. Grams.	IV. Yield of methylamine calculated from III after correction for ammonium chloride. Percentage of the theoretical yield.
13	3½	1½ hours at $234^{\circ}$	8.89	4.32	55.9
14	3½	2 " $260^{\circ}$	7.13	4.93	64.9
15	3½	2 " $260^{\circ}$	7.48	5.14	68.0
16	2½	2 " $240^{\circ}$	11.27	4.59	59.9
17	2½	2 " $260^{\circ}$ (reached $270^{\circ}$ )	12.15	4.52	58.6

*Effect of Ammonium Sulphate on the Transformation.*—Table V summarises the results of a study of the effect on the yield of methylamine of the duration of heating and of the presence during the reaction of different proportions of ammonium sulphate. In this series, the percentage of methylamine was determined by François' method, already referred to, in that portion of the amine hydrochlorides which was dissolved by alcohol, but undissolved by chloroform.

*Estimation of the Dimethylamine and Trimethylamine in the Chloroform-soluble Part.*—The following percentages of dimethylamine and trimethylamine hydrochlorides were found in the chloroform-soluble portions obtained in experiments 19 and 24, using Bertheaume's method (*Compt. rend.*, 1910, 150, 1251), that is, by precipitating the trimethylamine as periodide and estimating volumetrically the trimethylamine in the precipitate and the dimethylamine in the solution:

	Dimethylamine hydrochloride. Per cent.	Trimethylamine hydrochloride. Per cent.
Chloroform-soluble portion from experiment 19 .....	67.4	64.8
Chloroform-soluble portion from experiment 24 .....	27.0	31.6

Although the comparison is not complete, since in experiment 28 the percentage of methylamine in the chloroform-insoluble portion was not estimated, the results tabulated above indicate that two equivalents of ammonium benzenesulphonate are as effective as four. With the larger proportion of ammonium benzenesulphonate, the mixture did not fuse so readily.

*Examination of the Residual Benzenesulphonate.*—In experiment 25, the amines were liberated by the addition of baryta, the excess of which was removed from the residue in the distilling flask after the distillation by means of carbon dioxide. The solution was then evaporated to dryness, and the barium estimated in the dried product.

Found: Ba = 30.7.

$(C_6H_5SO_3)_2Ba$  requires Ba = 30.4, and  $C_6H_4(SO_3)_2Ba$  requires Ba = 36.7 per cent.

*General Comparison of Experiments made at about 260°.*—In table VII are assembled those experiments in which ammonium methyl sulphate was heated for different periods at about 260°, with and without the addition of ammonia or of an ammonium salt. Two experiments made in closed vessels (29 and 30) are included.

TABLE V.

12.9 Grams of ammonium methyl sulphate were heated in each experiment. One equivalent of ammonium sulphate = 1/20 mol. = 6.6 grams. Experiments 18—23 were made simultaneously, using the same oil-bath, which was heated from the ordinary temperature. The temperatures are those of the bath.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	
No. of experiment.	Weight of ammonium sulphate added. Grams.	Duration of heating. Hours.	Temperature.	Weight of amine hydrochlorides dissolved by alcohol but undissolved by chloroform. Grams.	Percentage of methylamine hydrochloride by analytical estimation in substance (col. IV) by undissolved by chloroform.	Yield of methylamine calculated from III after correction for ammonium chloride. Percentage of theoretical yield.	Yield of methylamine calculated from IV after correction for ammonium chloride. Percentage of theoretical yield.	Yield of methylamine by analytical estimation of ammonium methylamine chloride. (IV and V).
18	None	1½	¾ hour at 260°	4.57	2.74	59.6	32.4	26.8
19	6.6	1½	"	4.99	3.14	65.8	38.4	32.8
20	13.2	1½	"	4.81	3.01	63.1	36.4	27.5
21	None	3	2¼ hour at 260°	4.54	2.63	59.1	30.8	24.6
22	6.6	3	"	4.49	3.02	58.3	36.3	31.5
23	13.2	3	"	4.74	2.95	62.1	35.6	30.0
24	66.0 (10 equivalents)	2	1 hour at 260°	4.39	2.89	56.9	34.7	29.6

*Effect of Ammonium Benzenesulphonate on the Transformation.*  
TABLE VI.

12.9 Grams of ammonium methyl sulphate were heated in each experiment, except in experiment 25, where 6.45 grams were used and other substances in proportion. The figures shown in the table for experiment 25 are the actual figures multiplied by two to facilitate comparison. One equivalent of ammonium benzenesulphonate = 17.5 grams.																
I.		II.		III.		IV.		V.		VI.		VII.		VIII.		
No. of experiment.	Weight of ammonium benzenesulphonate added. Grams.	Duration of heating.	Temperature.	Weight of amino hydrochlorides dissolved by alcohol.	Weight of amine hydrochlorides dissolved by alcohol.	Percentage of methylamine by analytical estimation in substance (col. IV) by undissolved chloroform.	Yield of methylamine calculated from III after correction for ammonium chloride.	Yield of methylamine calculated from IV after correction for ammonium chloride.	Yield of methylamine by analytical estimation of ammonium methylamine chloride. (IV and V). Percentage of theoretical yield.							
25	17.5	1½ hours	Heated from ord. temp. 20 min. at 250°-260°.	4.82	3.68	—	63.3	46.4	—							
26	35.0	1½ "	Heated from ord. temp. 55 min. at 250°-260°.	5.02	4.35	75.5	66.2	56.3	48.7							
27	35.0	18 min.	Ammonium methyl sulphate added to ammonium benzenesulphonate and heated to 250°-260°.	4.52	3.89	—	58.8	49.5	—							
28	70.0	1½ hours	Heated from ord. temp. 1 hour at 250°-260°.	5.24	4.29	—	71.0	55.4	—							

12.9 Grams of ammonium methyl sulphate were heated in each experiment, except in experiment 25, where 6.45 grams were used and other substances in proportion. The figures shown in the table for experiment 25 are the actual figures multiplied by two to facilitate comparison. One equivalent of ammonium benzenesulphonate = 17.5 grams.

TABLE VII.

No. of experiment.	I.	II.	III.	IV.	V.	VI.
	Addition.	Duration of heating.	From titra- tion.	From amine hydro- chloride soluble in alcohol after correc- tion for ammonium chloride. Yield of methylamine as percentage the theoretical yield.	From amine hydro- chloride soluble in alcohol but insoluble in chloroform after correc- tion for ammonium chloride. Yield of methylamine as percentage the theoretical yield.	By analytical estimation of the methyl- amine.
12	None.	16 min.	—	43.3	30.1	—
11	"	17 "	—	47.3	28.0	—
3	"	30 "	89.6	54.1	—	26.8
18	None (closed vessel).	14 hours.	—	59.6	32.4	—
29	None.	11 "	—	58.5	33.3	—
21	Ammonia.	31 "	—	59.1	30.8	24.6
14	"	34 "	—	64.9	—	—
15	1 equivalent $(\text{NH}_4)_2\text{SO}_4$ .	3 "	—	68.0	38.4	32.8
19	1 equivalent $(\text{NH}_4)_2\text{SO}_4$ .	14 "	—	65.8	34.8	—
30	1 (closed vessel).	14 "	—	56.0	—	—
22	1 equivalent $(\text{NH}_4)_2\text{SO}_4$ .	3 "	—	58.3	36.3	31.5
20	2 equivalents $(\text{NH}_4)_2\text{SO}_4$ .	14 "	—	63.1	36.4	27.6
23	"	3 "	—	62.1	35.6	30.0
24	10 equivalents $(\text{NH}_4)_2\text{SO}_4$ .	2 "	—	56.9	34.7	29.6
25	1 equivalent $\text{C}_6\text{H}_5\text{SO}_2\text{NH}_4$ .	14 min.	—	63.3	46.4	—
27	2 equivalents $\text{C}_6\text{H}_5\text{SO}_2\text{NH}_4$ .	18 "	—	58.8	49.6	—
26	"	14 hours.	—	66.2	56.3	48.7
28	4 equivalents $\text{C}_6\text{H}_5\text{SO}_2\text{NH}_4$ .	14 "	—	71.0	55.4	—

*Methylamine from a Mixture of the Sulphates of Ammonium, Dimethylammonium, and Trimethylammonium.*—Five grams of the mixed hydrochlorides of dimethylamine and trimethylamine, obtained in the extractions with chloroform, were mixed with an excess of sodium hydroxide solution, and the liberated bases were distilled into an aqueous solution of 6 grams of sulphuric acid. The solution was neutralised with ammonia (but the presence of some free acid would doubtless have been advantageous), and the residue, after evaporation to dryness, was heated at 270° for a short time. The bases were converted into the hydrochlorides and extracted with alcohol, and then with chloroform, which dissolved 1.55 grams. After purification of the portion insoluble in chloroform, 0.44 gram of methylamine hydrochloride was obtained.

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### XXX.—*The Behaviour of the Constituents of Banded Bituminous Coal on Coking. Studies in the Composition of Coal.*

By RUDOLF LESSING.

THE four main constituents of banded bituminous coal have been isolated and described by Stopes (*Proc. Roy. Soc.*, 1919, [B], 90, 470) mainly from the microscopical and palæobotanical point of view, and designated by her fusain, durain, clarain, and vitrain respectively. These four ingredients, derived from the Thick Coal, Hamstead Colliery, have been chemically investigated recently by Tideswell and Wheeler (*T.*, 1919, 115, 619). Their researches comprised proximate and ultimate analysis, the action of solvents and of reagents on the four substances, and their destructive distillation in a vacuum with examination of the gaseous and liquid products. This vacuum distillation was carried out under conditions which yielded in each instance, not a coherent coke, but a solid residue consisting of loose particles little different in outward appearance from the original materials, although shrunk in total volume.

At the suggestion of Drs. Stopes and Wheeler, I investigated the behaviour of samples of fusain, durain, clarain, and vitrain upon coking in an apparatus previously described by me (*J. Soc. Chem.*

*Ind.*, 1912, **31**, 465, 671; *Trans. Inst. Gas Eng.*, 1912, 242; see also *J. Gas Lighting*, 1912, **118**, 815, 855). The method consists briefly in placing 1 gram of the coal sample into a cylindrical silica retort of approximately 1.25 cm. internal diameter and fitted with a side-tube 6.5 cm. from the bottom, and heating it in an electric furnace. A loosely fitting piston weighing 7.5 grams is placed on the coal charge, compressing it slightly, while allowing the gases and vapours to escape freely. These are led through the side-tube and a cotton-wool scrubber into a eudiometer.

Tideswell and Wheeler heated each sample for several days, raising the temperature by only 50° at a time in order to remove completely every trace of gas or liquid volatile at each stage of decomposition. The great difference in my procedure from theirs is that, apart from the coal being heated in a confined space, the whole period of carbonisation extends over a few minutes only, and that there is a considerable temperature gradient from the outside to the interior of the coal, at any rate during the first minute or two, which permits the re-condensation of some primary products of decomposition and their reaction with coal which has not yet undergone any considerable thermal change. By this reaction of an original or partly carbonised coal with primary products and the secondary decomposition of the latter, a coherent coke is formed.

This fundamental difference of the working conditions must be borne in mind when comparing the quantities and properties of products obtained by Tideswell and Wheeler with those found in this research.

The investigation was principally directed to ascertain any distinctions exhibited by the solid coking residues of the four coal constituents. The yields of liquid and gaseous products at the two temperatures employed, namely, 600° and 900°, were, however, also determined.

The samples originally submitted were fine powders passing through a 200-mesh screen. As was to be expected, the gas space between the particles of such powders was not sufficient to permit of the gas readily disengaging itself, especially during the evolution of the large volumes generated during the initial distilling period. It was therefore found that a few seconds after inserting the retort into the hot furnace a certain portion of coal dust was thrown up beyond the piston, passing between it and the retort wall, thus escaping carbonisation in the relatively cool upper part of the retort. This portion of the sample was finally weighed as carbon, producing a corresponding deficiency in the coke, tar, and gas figures. The small quantity of coal substance extracted from this





PLATE A.

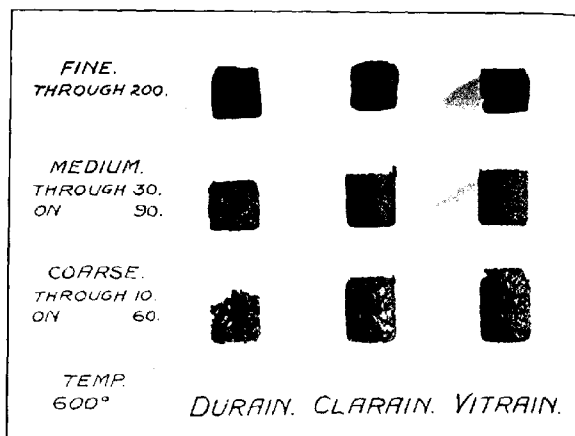
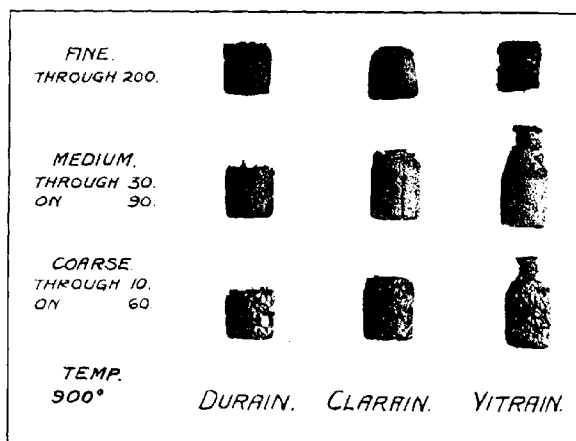


PLATE B.



4 5 Natural size.

[To face p. 24.]

portion with chloroform, and consequently weighed as tar, was regarded as negligible.

In order to avoid this drawback, another set of samples (except fusain, which was obtained almost exclusively as powder), which had been crushed to pass through 10 mesh and remain on 60 mesh, was kindly supplied by Dr. Wheeler. For the purpose of avoiding the fairly large spaces formed by the cohesion of these particles along comparatively few lines of contact, a third series of samples was prepared by crushing these specimens to a size passing through 30 mesh and remaining on 90 mesh. This size contained spaces large enough to allow free escape of gas, and left the solid particles in closer aggregate. These showed a higher sintering or agglutination effect, even under the slight pressure of the silica piston and with the short period of complete carbonisation, which are insignificant when compared respectively with the weight of superimposed coal, say, in a gas retort or coke-oven and with the duration of a large-scale charge, which may take as many hours or more as minutes are required in this test.

The results of the two series of experiments are recorded in tables I and II. The gas-production curves are shown in Figs. 1 and 2, and it should be noted that the volumes plotted could not be corrected for N.T.P. Photographs of the coke residues obtained are shown in 4/5 natural size in plates *A* and *B*.

*Coke Residues.*—The distinctive physical character of the coke obtained from the different specimens under varying conditions is the most interesting and important outcome of this research. The differences between fusain, durain, clarain, and vitrain already observed by Stopes and Wheeler are shown here in an accentuated form. The differences exhibited by the coke specimens from the four substances are not less remarkable than the consistency of properties observed with each one of them under varying conditions of size and heating. This constancy is even observable in details which appear somewhat obscured in the photographs, and particularly with the "fine" specimens.

*Fusain.*—Fusain shows no outward change in appearance after coking. It has no tendency whatever to adhere, and the solid coking residue is therefore a powder, like the original specimen. The particles retain their fibrous structure and dull black colour. No differences in appearance are observable between residues obtained at 600° and 900°.

*Durain.*—Durain undergoes practically no change of form during coking. The particles retain their angular shape and show little tendency to adhere to each other, although more than fusain. This applies particularly to the 600° series, and it was found impossible

to preserve a complete coke cylinder from the coarse specimen for photography. In several attempts, portions of the coke crumbled away, as shown in the photograph. At 900° the coke specimens are somewhat firmer, but in general durain must be regarded as practically devoid of any "coking value." The colour of the coke is the same dull, greyish-black as that of the original durain.

*Clarain.*—Clarain showed considerable fusion and merging of particles. At 900° most of the fine and medium-sized particles lost their identity almost completely, whilst even the coarse ones sintered or fused to rounded shapes which firmly cohered or fluxed together with their immediate neighbours. A peculiarity, which may or may not be significant, is that all clarain cokes made at 900° had a vertical crack which made them appear as of ellipsoid cross-section. They also showed a tendency to "mushroom" formation, which was, however, not as definite as in the vitrain specimens. All clarain cokes showed a peculiar brown sheen.

*Vitrain.*—The vitrain particles were well sintered and showed rounding of the angular edges, but the consolidation of particles did not go so far as with clarain. The colour is a silver-white of high lustre. The coke specimens from vitrain were the most distinctive in shape. This was of the "mushroom" type previously described (*loc. cit.*). It was remarkably definite at 900°, whilst the tendency of the lifting effect can be clearly seen on the specimens from the 600° tests. This phenomenon, which has not been observed in the use of other coking methods, is probably closely connected with the whole problem of the carbonisation of coal and the as yet unexplained discrepancy in the behaviour of various coals when subjected to thermal decomposition. As a plausible explanation, it is suggested that the formation of coke is due to the partial or complete fusion of coal or solutions of coal in tar or pitch primarily produced from adjacent coal particles, followed by an energetic thermal decomposition of the fused or sintered mass, by which its chemical constitution is altered, and further fusion is consequently arrested. According to the composition and the physical character of a coal or a coal constituent, these phases may follow each other in more or less rapid sequence, or may overlap very considerably.

In the case of vitrain, it appears that the phase of rigidity follows so rapidly after the fusion phase or overlaps it to such an extent that an impermeable wall is formed round the coal cylinder before the heat has penetrated to the inner core. As soon as this occurs and gasification proceeds, the gas pressure, overcoming the weight of the piston, throws up the core with explosive force in the only direction in which movement is possible. The pressure

having been released, the semi-rigid eruption is forthwith completely solidified, whilst the porosity of the whole specimen increases sufficiently for the ready release of the gas made during the remainder of the carbonising period. It is interesting to note that

TABLE I.

*Temperature, 600°.*

	Original Coals.			
	Fusain.	Durain.	Clarain.	Vitrain.
Coarse : Through 10 mesh on 60 mesh.				
				Per cent.
Coke .....		71.38	60.16	62.21
Carbon .....		—	0.46	0.29
Coke + Carbon .....		71.38	60.62	62.50
Tar .....		9.13	10.44	10.00
Gas (N.T.P.) .....		73 c.c.	96 c.c.	83 c.c.
Medium : Through 30 mesh on 90 mesh.				
Coke .....		71.18	60.18	62.21
Carbon .....		—	0.84	0.27
Coke + Carbon .....		71.18	61.02	62.48
Tar .....		8.38	11.46	10.75
Gas (N.T.P.) .....		76 c.c.	90 c.c.	81 c.c.
Fine : Through 200 mesh.				
Coke .....	—	—	—	—
Carbon .....	—	—	—	—
Coke + Carbon .....	81.42	67.22	65.36	65.80
Tar .....	3.56	8.35	8.86	5.88
Gas (N.T.P.) .....	64 c.c.	73 c.c.	80 c.c.	80 c.c.
Ash-free Dry Coals.				
	Fusain.	Durain.	Clarain.	Vitrain.
Coarse : Through 10 mesh on 60 mesh.				
Coke .....		83.16	69.36	72.39
Carbon .....		—	0.53	0.34
Coke + Carbon .....		83.16	69.89	72.73
Tar .....		10.64	12.04	11.64
Gas (N.T.P.) .....		85 c.c.	111 c.c.	97 c.c.
Medium : Through 30 mesh on 90 mesh.				
Coke .....		82.92	69.38	72.39
Carbon .....		—	0.97	0.31
Coke + Carbon .....		82.92	70.35	72.70
Tar .....		9.76	13.21	12.51
Gas (N.T.P.) .....		89 c.c.	104 c.c.	94 c.c.
Fine : Through 200 mesh.				
Coke .....	—	—	—	—
Carbon .....	—	—	—	—
Coke + Carbon .....	87.51	76.28	75.18	76.57
Tar .....	3.83	9.48	10.19	6.84
Gas (N.T.P.) .....	69 c.c.	83 c.c.	92 c.c.	93 c.c.

the eruption can be observed by the shock given to the tar vapours in the retort tube.

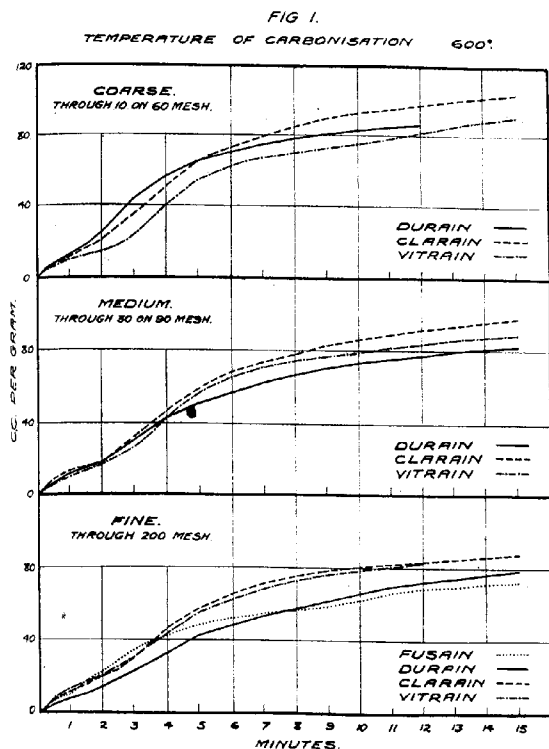
The phenomenon was also observed, but less markedly, at 600°, and to a still less degree with clarain.

TABLE II.

Temperature, 900°.

Original Coals.				
Fusain.	Durain.	Clarain.	Vitrain.	
Coarse: Through 10 mesh on 60 mesh.				
				Per cent.
Coke .....	65.74	54.34	54.66	
Carbon .....	2.58	0.62	0.56	
Coke + Carbon .....	68.32	54.96	55.22	
Tar .....	8.56	10.40	11.10	
Gas (N.T.P.) .....	182 c.c.	206 c.c.	209 c.c.	
Medium: Through 30 mesh on 90 mesh.				
Coke .....	62.56	54.06	54.96	
Carbon .....	2.06	0.60	0.66	
Coke + Carbon .....	64.62	54.66	55.62	
Tar .....	9.92	11.38	12.58	
Gas (N.T.P.) .....	190 c.c.	217 c.c.	221 c.c.	
Fine: Through 200 mesh.				
Coke .....	—	—	—	
Carbon .....	—	—	—	
Coke + Carbon .....	77.84	61.88	56.28	56.88
Tar .....	3.86	7.28	10.82	13.00
Gas (N.T.P.) .....	207 c.c.	184 c.c.	206 c.c.	194 c.c.
Ash-free Dry Coals.				
Fusain.	Durain.	Clarain.	Vitrain.	
Coarse: Through 10 mesh on 60 mesh.				
Coke .....	76.68	62.65	63.60	
Carbon .....	3.01	0.71	0.65	
Coke + Carbon .....	79.59	63.36	64.25	
Tar .....	9.97	11.99	12.91	
Gas (N.T.P.) .....	212 c.c.	238 c.c.	243 c.c.	
Medium: Through 30 mesh on 90 mesh.				
Coke .....	72.88	62.33	63.96	
Carbon .....	2.40	0.69	0.77	
Coke + Carbon .....	75.28	63.02	64.73	
Tar .....	11.55	13.12	14.64	
Gas (N.T.P.) .....	221 c.c.	250 c.c.	257 c.c.	
Fine: Through 200 mesh.				
Coke .....	—	—	—	
Carbon .....	—	—	—	
Coke + Carbon .....	83.66	70.23	64.73	66.19
Tar .....	4.15	8.26	12.45	15.12
Gas (N.T.P.) .....	222 c.c.	209 c.c.	237 c.c.	226 c.c.

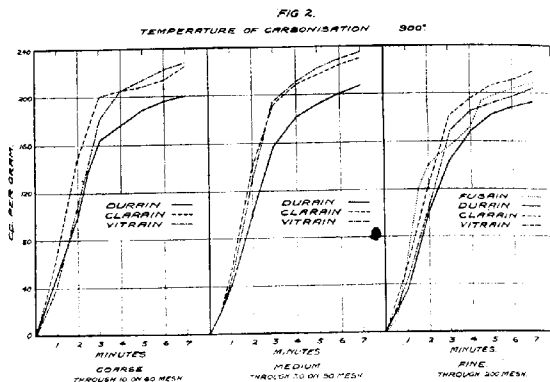
*Analytical Data.*—The carbonising results are recorded in tables I and II. As indicated above, the numbers for the "fine" specimens are practically valueless, on account of the loss or removal of uncarbonised coal from the hot zone. Whilst the gas and coke values are appreciably reduced, the loss of tar is partly compensated in some cases by the chloroform extract from the uncoked coal.



In considering the results from the "coarse" and "medium" specimens, it is to be seen that durain yields a much higher coke residue than clarain and vitrain, whilst the latter somewhat unexpectedly produces invariably a little more coke than the former.

An interesting feature is the amount of free carbon formed. At 900° this is considerably higher with durain than with clarain and vitrain, showing that the primary liquid products are more

susceptible to secondary decomposition or "cracking" at that temperature. On the other hand, at 600° no carbon whatever is produced from durain, whilst the amounts from clarain and vitrain are only slightly reduced (except in one case). This seems to indicate a considerable difference in the chemical nature of the primary decomposition products of durain on one side and of clarain and vitrain on the other. This observation is quite in accordance with Tideswell and Wheeler's assumption of varying proportions of "reactive" and "inert" groups in the different coal constituents. However, it is suggested that the very considerable discrepancies in the amount and composition of mineral ingredients (to be described in the succeeding paper) influences catalytically the course of primary and secondary decomposition, and may be at



any rate a contributory factor of the degree of reactivity of coal substance. The carbon may also be regarded as a measure of the amount of pitch formed primarily from each substance.

The behaviour of clarain and vitrain is fairly similar, although their products of decomposition show sufficient numerical differences to account for the physical distinction of their coke residues. The gas yield of clarain and vitrain is almost equal, and in all cases larger, than that of durain. The differences in gas yield at 900° are much less pointed than those at 600°. This is due to the secondary decomposition of heavy hydrocarbons and cracking of tar oils running back into the hot zone. All samples of gas contained hydrogen sulphide and burned with a luminous flame, the order of luminosity being clarain, vitrain, durain, fusain.

## EXPERIMENTAL.

The electric furnace employed for heating the retort tube has been somewhat modified from that originally described. It consists of two vertical silica tubes wound in series with nichrome wire of the same length and gauge on each tube. The furnace tubes are open at both ends, and by a height-adjusting attachment the coal charge may be placed in any desired portion of the heating tube. In all experiments here described, the retort was fixed with the coal charge in the middle of the heating tube, thus being in the hottest part of the tube. Care was taken to avoid the indraught of cold air into the furnace tube by placing asbestos collars at each end. In the second heating tube was placed a calibrated platinum-platinum-iridium thermocouple with the junction in a position corresponding with the centre of the coal charge in the other tube. Before making a test, the furnace was heated until a constant temperature was attained. The constancy of temperature in both tubes was frequently checked by transferring the thermocouple from one tube to the other, when only negligible differences in temperature were detected.

After inserting the coal sample and silica piston in the retort tube, it was connected to the scrubber and eudiometer, the latter being filled with a mixture of glycerol and water. The air in the retort and scrubber was not removed, as only total volumes were read and no gas analyses were made. When ready, the retort was plunged into the furnace tube, when distillation quickly began. Readings of the volumes of gas generated were made at intervals of half a minute.

At the end of the distillation period, the retort tube was removed from the furnace, but left connected to the eudiometer until the gas had attained the ordinary temperature. The final measurement of the gas was then made, the eudiometer disconnected, and the scrubber and retort tube containing the coke were extracted with chloroform for the removal of tar. The chloroform extract was evaporated and dried, and the residue weighed; the coke was also weighed after drying. Small quantities of retort carbon produced by the decomposition of tar vapours on the hot retort walls were weighed separately.

The temperatures selected for treating the specimens were 600° and 900°. The former is the maximum temperature which Tideswell and Wheeler employed in their experiments. The latter was chosen as likely to produce greater changes in the solid coking residues and as more nearly approximating the temperatures customarily employed in industrial carbonising methods. The



three sets of specimens differing in size of particles only of durain, clarain, and vitrain, and fusain of original size, were submitted to tests at both temperatures in a strictly comparative fashion.

At 900°, a heating period of exactly seven minutes was employed, beyond which the evolution of gas became very slow. It should be stated that in experiments extended for longer periods it never ceased entirely, which is to be explained by the fact that under the conditions of working, part of the liquid products was able to run back into the hot zone of the retort, where they are again and again subjected to gasification by secondary thermal decomposition or "cracking." The volume of gas thus generated is fairly constant.

In the tests at 600°, it was found necessary to prolong heating to fifteen minutes, after which the gas-production curves become practically straight horizontal lines.

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### XXXI.—*The Mineral Constituents of Banded Bituminous Coal. Studies in the Composition of Coal.*

By RUDOLF LESSING.

THE peculiar behaviour on carbonisation of fusain, durain, clarain, and vitrain described in the preceding paper made it appear possible that the differences observed were not entirely due to the composition of their organic constituents, but that they were at any rate influenced or accentuated by the catalytic effect of their mineral components. The influence of catalysts on the spontaneous combustion and particularly on the carbonisation of coal was discussed at length in the William Young Memorial Lecture of 1914 (Lessing, "Catalysis in the Gas Industry," *Trans. North Brit. Ass. of Gas Managers*, 1914, 65; *J. Gas Lighting*, 1914, 77, 570), and a good deal of evidence goes to show that the "ash" contents of coal play an important rôle in its thermal decomposition. By inference it may be assumed that the mineral contents of decaying vegetable matter, and adventitious inorganic material in contact therewith, have likewise exerted an influence on the formation of coal or its constituents. Experiments in connexion with an investigation of the coal-washing process, hitherto unpublished, have shown that the frac-

tions separable from coal slack by washing differ vastly, not only in the amount, but in the nature of the mineral matter which they contain. It seemed, therefore, interesting and promising to study the ash contents of fusain, durain, clarain, and vitrain, particularly as casual tests had shown that they differed considerably in appearance. For the purpose of this work Dr. Wheeler kindly supplied further large samples of the three substances which were required to make quantitative analyses possible. Durain and clarain were in pieces up to 30 mm. cube, vitrain in pieces of 5–10 mm. cube. Fusain was extracted from a large sample of the original coal which, like that used in the preceding research, came from the Thick Coal seam, Hamstead Colliery.

*Percentage of Ash.*—In view of discrepancies between the preliminary tests and some of Tideswell and Wheeler's ash figures (particularly for fusain and durain), and the probability that the inorganic constituents were not evenly distributed throughout the coal, the samples were not crushed and mixed as is usual in commercial analysis, but one or more individual pieces were ignited for each test. In table I the results obtained from the original samples (1 gram) and those of the bulk samples are given, together with the weight of sample used for individual tests.

TABLE I.

	Fusain.		Durain.		Clarain.		Vitrain.	
	Sample.	Ash.	Sample.	Ash.	Sample.	Ash.	Sample.	Ash.
	Grams.	cent.	Grams.	cent.	Grams.	cent.	Grams.	cent.
"Fine" sample	1.0000	4.48	1.0000	4.94	1.0000	1.38	1.0000	1.16
"Coarse" sample			1.0000	7.22	1.0000	1.58	1.0000	1.16
Bulk sample. ...	5.9642	16.70	10.4024	5.68	11.4416	0.91	7.1680	1.07
	7.0522	14.66	12.1436	5.89	10.3068	1.13	11.2622	1.18
			11.9188	7.15	12.4234	1.49	11.1180	1.10
					12.5904	1.28	10.0082	0.98
					13.7908	1.17	10.0000	1.22
					13.2226	1.37		
					12.2544	1.22		
					13.3457	1.18		
	13.0164	15.59	34.4648	6.26	99.3757	1.22	49.5564	1.11

It will be noticed that the percentage of ash in clarain and vitrain is fairly constant, particularly when allowance is made for the enhanced experimental error in dealing with small percentages. The variation of the ash contents of durain is much more marked, although the percentage discrepancy to be calculated is not appreciably increased over that of clarain. Fusain, however, shows very considerable discrepancies between different samples. Apart from

the results from fusain given in table I, of which the "fine" sample was used in the preceding research and the bulk sample in the following analyses, amongst some picked samples, one was found containing as much as 28.75 per cent. of ash. The cause of these discrepancies is discussed below.

*Appearance of Ash.*—The ashes which were prepared by ignition of the samples in a muffle furnace on silica dishes at low temperature showed considerable difference in colour. The ash from fusain was dark brownish-grey, that from durain pure pale grey without the slightest brown tint, that from clarain a reddish-brown biscuit, and that from vitrain a pale biscuit colour. The large lumps were ignited uncrushed, and in the course of burning off produced lamina-

TABLE II.

*Fusain.*

	Soluble in water. Per cent.	Soluble in HCl. Per cent.	Insoluble in HCl. Per cent.	Total. Per cent.
SiO <sub>2</sub> .....	Nil	0.78	8.06	8.84
Al <sub>2</sub> O <sub>3</sub> .....	0.19	8.33	4.06	8.66
Fe <sub>2</sub> O <sub>3</sub> .....				3.37
MnO .....				0.51
TiO <sub>2</sub> .....				0.04
CaO .....	10.03	46.64	0.33	57.00
MgO .....	0.41	0.89	Nil	1.30
Na <sub>2</sub> O .....	0.65	2.59	—	3.24
K <sub>2</sub> O .....	0.14	0.53	—	0.67
SO <sub>3</sub> .....	4.71	9.17	0.77	14.65
P <sub>2</sub> O <sub>5</sub> .....	—	—	—	—
CO <sub>2</sub> .....	0.53	2.45 (diff.)	—	2.98
Total .....	16.66	71.38	13.22	101.26
Total by direct weighing	16.57	71.38	12.05	100.00

*Durain.*

	Soluble in water. Per cent.	Soluble in HCl. Per cent.	Insoluble in HCl. Per cent.	Total. Per cent.
SiO <sub>2</sub> .....	Trace	1.46	49.08	50.54
Al <sub>2</sub> O <sub>3</sub> .....	Trace	19.94	24.20	42.34
Fe <sub>2</sub> O <sub>3</sub> .....				1.36
MnO .....				Nil
TiO <sub>2</sub> .....				0.44
CaO .....	1.47	1.85	0.37	3.69
MgO .....	Nil	Nil	Nil	Nil
Na <sub>2</sub> O .....	Nil	Nil	Nil	Nil
K <sub>2</sub> O .....	Nil	Nil	—	Nil
SO <sub>3</sub> .....	2.10	0.98	0.15	3.23
P <sub>2</sub> O <sub>5</sub> .....	—	—	—	—
Total .....	3.57	24.23	73.80	101.60
Total by direct weighing	3.48	23.81	72.71	100.00

TABLE II (continued).

<i>Clarain.</i>				
	Soluble in water. Per cent.	Soluble in HCl. Per cent.	Insoluble in HCl. Per cent.	Total. Per cent.
SiO <sub>2</sub> .....	0.12	0.96	8.36	9.44
Al <sub>2</sub> O <sub>3</sub> .....	0.10	12.66	7.86	16.58
Fe <sub>2</sub> O <sub>3</sub> .....				3.31
MnO .....				0.23
TiO <sub>2</sub> .....				0.50
CaO .....	10.50	1.94	0.54	12.98
MgO .....	9.20	1.32	Nil	10.52
Na <sub>2</sub> O .....	13.76	1.95	—	15.71
K <sub>2</sub> O .....	Nil	Nil	—	—
SO <sub>3</sub> .....	31.73	0.45	—	32.18
P <sub>2</sub> O <sub>5</sub> .....	Nil	0.01	Nil	0.01
Total .....	65.41	19.29	16.76	101.46
Total by direct weighing ...	65.24	17.86	16.90	100.00

<i>Vitrain.</i>				
	Soluble in water. Per cent.	Soluble in HCl. Per cent.	Insoluble in HCl. Per cent.	Total. Per cent.
SiO <sub>2</sub> .....	Trace	0.76	5.32	6.08
Al <sub>2</sub> O <sub>3</sub> .....	3.11	13.44	2.40	15.49
Fe <sub>2</sub> O <sub>3</sub> .....				3.09
MnO .....				0.13
TiO <sub>2</sub> .....				0.24
CaO .....	12.42	2.46	0.34	15.22
MgO .....	1.04	0.83	Nil	1.87
Na <sub>2</sub> O .....	16.12	1.55	—	17.67
K <sub>2</sub> O .....	0.20	Nil	—	0.20
SO <sub>3</sub> .....	28.62	1.49	0.78	30.89
P <sub>2</sub> O <sub>5</sub> .....	—	—	—	Trace
CO <sub>2</sub> .....	6.69	—	—	6.69
Total .....	68.20	20.53	8.84	97.57
Total by direct weighing...	69.52	20.46	10.02	100.00

tion, which it is suggested occurs parallel to the bedding plane of the coal. Clarain ash invariably contained intrusions of grey plates, indicating the presence of durain (or possibly fusain particles, this yielding a similar but darker grey ash). Vitrain ash contained also occasionally grey laminae and some red, ferruginous specks. These foreign particles were picked out and rejected for analysis.

*Analysis of Ash.*—In view of the limited supply and the small ash content of the specimens, the complete analysis of the ashes presented considerable difficulties, as each had to be carried out on 0.5 gram. In the case of durain and clarain analyses could be repeated, but this was not possible in the case of vitrain. However,

it was considered advisable to record the figures as obtained, as they typify in their main aspect the character of the mineral constituents of vitrain and distinguish it clearly from durain, whilst showing considerable similarity with clarain.

The ashes were first separated into fractions soluble in water, soluble in hydrochloric acid and insoluble in hydrochloric acid. The water-soluble and hydrochloric acid-insoluble fractions were weighed after evaporation and drying. The hydrochloric acid-soluble portions could not be weighed directly on account of the formation of chlorides of the alkalis and alkaline earths, and were determined by difference. Each of the fractions was analysed separately, but the ammonia precipitates (oxides) of all three had to be combined.

The results are recorded in table II, and show very considerable differences between the four ashes. This is apparent both from the actual composition and the ratios of portions soluble and insoluble in water and acid.

*Fusain.*—The most striking feature of fusain ash is its high percentage of lime, amounting to 57·00 per cent. This is responsible for the high amount of soluble matter in this ash. Much of this lime is present as calcium oxide, and the ratio of the amount soluble in water and in acid is probably variable according to the amount of water used for extraction. The aqueous solution attracts carbon dioxide from the air, for which allowance has been made in the analysis. The actual free alkalinity corresponds with 6·7 per cent. of calcium oxide, the balance of which is present as calcium sulphate. Some sulphur may have been introduced in these analyses from the gas used for ashing the samples and in heating the alkali fusion of the insoluble portion.

*Durain.*—Nearly three-quarters of durain ash is insoluble in water or acid. The water-soluble portion amounts only to 3·5 per cent., which consists of calcium sulphate. The bulk of this ash consists of an aluminium silicate of the approximate composition of clay substance. The complete absence of manganese, magnesia, and alkalis calls for comment. The water extract of durain ash has a neutral reaction.

*Clarain.*—The soluble portion of clarain ash is almost as high as that of vitrain ash. It differs, however, from the latter in its lower percentage of lime. It is the only ash containing considerable amounts of magnesia, which is worthy of note in view of the importance of magnesium as a vital constituent of chlorophyll. It is also fairly high in soda, but contains no trace of potash. Iron is present in a sufficient quantity to account for the biscuit colour. Clarain ash has an alkaline reaction, and its alkalinity corresponds with 5·41 per cent. of sodium carbonate.

*Vitrain*.—Vitrain ash is somewhat similar to clarain ash, but shows some distinct differences. It contains the lowest percentage of insoluble matter as well as the lowest amount of silica of all four ashes. A distinct difference from clarain is the low magnesia figure. Practically all the lime is present as sulphate; soda is high, and part of it is present as sulphate, another part as carbonate. The high percentage of water-soluble substances accounts for a tendency of some particles to melt at the temperature of ignition. The small amount of matter insoluble in acid is in accordance with the absence of débris from this ingredient observed by Stopes, and with its probable colloidal nature. The alkalinity of vitrain ash corresponds with 5.19 per cent. of sodium carbonate.

#### *Discussion of Results.*

The fact that different portions of one and the same lump of coal contain different amounts of mineral matter is obvious and well known to all who have to deal with the analysis of coal, ever since de Marsilly (*Compt. rend.*, 1848, 46, 882) observed "that however pure a piece of coal may be, and however homogeneous it may appear to the eye, its different parts do not yield the same proportions of fixed residue on incineration." Many thousands of analyses of the ash of different portions of a coal-seam must have been made from time to time for commercial purposes, the results of which have not been published. There are, however, on record comparatively few analyses of the ash of clearly defined constituents of coal, such as the composition of the ash of "mineral charcoal" (fusain) from Better Bed and Haigh Moor reported by Thorpe ("Coal, its History and Uses," 1878).

The separation by Stopes of four distinct ingredients from bituminous coal made it possible to inquire more closely into their mineral constituents. Kendall pointed out (*Rep. Brit. Assoc.*, Newcastle, 1916, 395) that there are three sources of mineral matter in coal, the mode of distribution of which is of great economic consequence, some being separable and others not, namely: (1) The residue of the mineral constituents of the plants composing the coal; (2) detrital matter blown or washed into the deposit; (3) the calcite, iron pyrites, etc., segregated as veins in the seams.

In amplification of this statement Stopes and Wheeler ("Monograph on the Constituents of Coal," 1918) discuss the probability that part of the inherent ash in plants may be lost in the process of coal formation, a fact which renders the problem of identification of individual coal constituents still more complex.

In view of the small amounts of material handled in this research,

and the complex analytical procedure followed, it is somewhat speculative to form definite conclusions as to the relation which the elements in these ashes have to each other, and still more so as to the combination in which they occur in the original coal before incineration.

It seems quite inadmissible to go yet further and postulate on the relationship of the ashes to the mineral constituents in the plants from which the coal has been formed. Any suggestions of a theoretical nature in this state of ignorance must, therefore, be regarded as tentative and require further proof by the analysis of ashes from a great variety of coals and their components, instead of relying on the present results obtained from one particular coal.

Moreover, the ashes, even after "hand picking" of particles obviously belonging to one of the other groups, were by no means homogeneous mixtures, but specks of white and reddish-brown substances could be easily discerned in the biscuit coloured or grey bulk. They no doubt represent the ash of individual plant fragments or mineral intrusions (lime, pyrites) in the coal substance.

The results are, however, considered definite enough to indicate the following suggestions:

*Fusain*.—The large proportion of lime and soluble matter makes it highly probable that the bulk of this ash is due to infiltration of lime salts, most likely in the form of calcium hydrogen carbonate, and that this is present in the fusain as calcium carbonate, more or less evenly distributed throughout the porous substance of this "mineral charcoal." Such infiltration would explain the discrepancy of ash percentage observed in various samples of fusain. The infiltration theory finds support by some experiments on the direct extraction with hydrochloric acid of fusain before incineration. Three samples were used, one of them being identical with the "fine" sample of table I, another being similar to the bulk sample, and a third consisting of a lump of fusain about 20 mm. long by 10 mm. thick. On warming these samples with the acid, a copious liberation of carbon dioxide took place. The following percentage figures were obtained:

	(1.)	(2.)	(3.)
Total ash .....	4.48	13.30	28.75
Extracted by hydrochloric acid from coal .....	19.96	47.07	40.70 of ash.
Extracted by hydrochloric acid from remaining ash .....	13.08	20.83	14.09    "
Insoluble .....	66.96	32.10	45.21    "

The differences in solubility are no doubt due to the presence of varying proportions of pyrites which may or may not be similarly caused by infiltration.

The presence of large amounts of calcium carbonate in fusain suggests comparison with the composition of the petrifications known as "Coal Balls" (Stopes and Watson, *Phil. Trans.*, 1908, [B], **200**, 167). These, however, always contain about 10 per cent. of magnesia, whilst this is present to a small extent only in fusain ash. It is also worthy of note that the thin veins of white mineral found along the cleavage planes contain from 40 to 45 per cent. of calcium carbonate. This further supports the view that infiltration of calcium salts has taken place at one period of the formation of the coal seam through cracks or between the stratified layers and into the very porous structure of the fusain particles.

*Durain.*—The composition of durain is comparatively simple, since many of the minor constituents are entirely absent and others only small in quantity. It consists to the extent of 93 per cent. of alumina and silica. The presence of a large percentage of alumina in the ash from plants or plant products suggests at once the presence of, or origin from, lycopods, which are characterised by a high aluminium content. This important property of lycopodia was shown by Aderholt (*Annalen*, 1852, **82**, 111), Ritthausen (*J. pr. Chem.*, 1853, **58**, 134), Church (*Chem. News*, 1874, **30**, 137), and more recently by a comparative study of many other species by Kratzmann (*Sitzungsber. K. Akad. Wiss. Wien*, 1913, **122**, 311).

Since the lycopods are regarded as largely forming the bulk of the coal measures, the high alumina percentage in durain would be in accordance with paleobotanical and other evidence.

However, the absence of alkalis, magnesia, and the low lime figure call for caution. Moreover, it so happens that the ratio of alumina and silica is practically identical with that obtaining in "clay substance" (kaolinite,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ). The colour of fusain ash is a pure grey and almost white, thus proving the freedom from the colour-giving constituents which one would expect in the ash from plant fragments, but their absence may be due to their removal from the original plant substance during the course of coal formation. It was, therefore, considered useful to compare the ratio  $\text{Al}_2\text{O}_3 : \text{SiO}_2$  in lycopodia amongst themselves and with that obtaining in coal constituents and "clay substance." The values on p. 264 were obtained.

Whilst one might suspect that the mineral constituents in present-day plants differ from those grown in a palaeozoic climate and habitat, this  $\text{Al}_2\text{O}_3 : \text{SiO}_2$  ratio indicates that the fusain and durain are in an entirely different class from the clarain and vitrain. The latter gave a ratio which is quite comparable with that of the ash of lycopodia, but the ratio in the former differs very considerably. It is so close to the ratio in "clay substance" that one is forced to



	Percentage in ash.		$\text{Al}_2\text{O}_3$ SiO <sub>2</sub>
	$\text{Al}_2\text{O}_3$	SiO <sub>2</sub>	
<i>L. chamaecypar</i> , with spores (Aderholt) ...	51.85	13.60	3.81
"    without spores (Aderholt) ...	57.36	12.96	4.43
<i>L. clavatum</i> (Aderholt) .....	26.65	13.94	1.91
"    (Ritthausen) .....	39.07	18.82	2.11
"    " .....	22.20	13.01	1.71
"    " (Church) .....	15.24	6.40	2.38
<i>L. complanatum</i> (Ritthausen) .....	37.87	10.06	3.76
<i>L. alpinum</i> (Church) .....	33.50	10.24	3.27
<i>L. selago</i> (Church) .....	7.29	2.53	2.88
Average ratio .....			2.92
"Mineral charcoal"—			
"Better Bed" (Thorpe) .....	33.8	38.7	0.87
"Haigh Moor" (Thorpe) .....	28.7	36.1	0.80
Fusain (Lessing) .....	8.66	8.84	0.98
Durain " .....	42.34	50.54	0.84
Clarain " .....	16.58	9.44	1.76
Vitrain " .....	15.49	6.08	2.55
Kaolinite (calcined) (Theory) .....	45.87	54.13	0.85

assume the presence of clay or a silicate of the same composition in durain and fusain. Whether this silicate was deposited in the plant or was produced like clay from rocks during the formation of the coal is impossible to say. The observation by Stopes that the mass of plant fragments in durain consists of spores embedded in a matrix of granular material makes it not impossible that the silica may be derived from earthy matter with which the spores originally became contaminated.

*Clarain and Vitrain*.—The composition of the ashes of these two substances make it very probable that they represent mainly the remainder of the original plant ashes. Both contain considerable quantities of alkali, are high in sulphur (which is largely due to the retention of organic sulphur by the alkali), and have a fairly uniform percentage of total ash. The alumina in both suggests their derivation from lycopodia, and, as appears from the above, the  $\text{Al}_2\text{O}_3$  : SiO<sub>2</sub> ratio agrees quite well with that found in some of the existing species. Moreover, the bulk of the alumina in clarain and even more so in vitrain is soluble in acid in contradistinction from the alumina in durain, of which the greater portion is insoluble in acid.

The two ashes are very similar save in one respect, namely, the magnesia content. Clarain contains as much as 10.52 per cent. of magnesia, as against 1.87 per cent. in vitrain and a similar amount in fusain. Whilst no direct inference can be drawn from this fact, the magnesia suggests the presence of degradation products of leaf substance containing chlorophyll in clarain. Stopes (*Proc. Roy. Soc.*, 1919, [B], 90, 480) found that "the clarain is the portion

most interesting to the palaeobotanist, for in it lies the greatest variety of recognisable plant tissues and structures. There may be in it clear bands and zones showing each disintegrated plant substance, also bands of clear cuticle, spore exines, resin bodies, and other structures, and among this variety of material plant stem tissues, leaf-tissues and so on may be preserved and may even fill the whole area of sections."

The proved presence of leaf-tissues in clarain and of magnesia in its ash may be a mere coincidence. Indeed, it is somewhat difficult to account for the quantities found. According to Willstätter, green leaves contain on an average 0.8 per cent. of chlorophyll, which in its turn yields 4.5 per cent. of pure magnesia on incineration. The magnesia may rise to 8 per cent. in etiophyllin. Even allowing for a considerable concentration of magnesia during the process of coal formation, these amounts are scarcely large enough to account for the percentage found without resorting to speculation on a higher chlorophyll and magnesia content in palaeozoic plants or on an accumulation of magnesia from successive generations of leaves. It is, however, considered worth while to draw attention to this peculiar distinction of clarain from the other constituents.

#### *Conclusion.*

The results obtained from this research can only be considered as of a preliminary nature, and are recorded mainly in order to stimulate research in this direction, which can only be successful if a great variety of coals are investigated by "rational" analysis. Refining of coal by washing is still in a crude stage on account of lack of knowledge of the distribution of the ash. Evidence exists that differences in the amount and composition of inorganic constituents in coal can direct the course of its thermal and probably spontaneous decomposition. It is further likely that the course of formation of coal and its main constituents has been similarly influenced by plant debris and adventitious impurities. More detailed knowledge of the mineral constituents in coal is, therefore, required, both from the theoretical and technical point of view.

In conclusion, I wish to express my thanks to Dr. Marie C. Stopes and Dr. R. V. Wheeler, who laboriously prepared most of the samples for me, and who assisted the investigations with much suggestive criticism, and to Mr. A. H. Raine, who has carried out the experimental work for this and the preceding paper.

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XXXII.—*l*-Hexylsuccinic Acid.

By HENRY WREN and HENRY BURNS.

THE interesting observations which had been made during the investigation of the racemisation of the optically active phenylsuccinic acids and their derivatives (Wren and Williams, T., 1916, 109, 572; Wren, T., 1918, 113, 210) appeared to render it desirable to examine the behaviour of a similar compound in which the phenyl group was displaced by an alkyl radicle of approximately the same weight. This was more particularly the case since, although a general survey of the literature would lead to the conclusion that the presence of a phenyl group directly united to the asymmetric carbon atom of a racemisable compound renders the substance more prone to racemisation than does a similarly placed alkyl group, a precise comparison of the effect under similar conditions does not appear to have been made. For this purpose, hexylsuccinic acid was selected. Circumstances have combined, however, to prevent the work being carried to completion, and as its continuation must be postponed for some considerable time, it was considered desirable to give the present short account of the resolution of the racemic acid and of the properties of *l*-hexylsuccinic acid.

## EXPERIMENTAL.

*n*-Hexylsuccinic acid (28 grams; prepared according to the directions of Higson and Thorpe, T., 1906, 89, 1469) and quinine (52.1 grams) were dissolved by gentle warming in ethyl alcohol (560 c.c.). Tufts of small needles slowly separated from the solution at the ordinary temperature, which, when air-dried, weighed 44 grams. The salt was purified by repeated crystallisation from alcohol, 20 c.c. of the solvent being used for each gram of material. The course of the resolution was followed by determining the specific rotation of the acid recovered from the successive filtrates, the observations being made in ethyl-alcoholic solution. In this manner, the following values were found: +12.97°, +7.55°, -2.44°, -8.7°, -13.7°, -17.3°, -20.2°, -22.6°, and -23.6°. The crop which had separated from the final mother liquor weighed 6.8 grams, and, on decomposition with dilute sulphuric acid and extraction with ether, gave 2.4 grams of *l*-hexylsuccinic acid, which melted at 81–83° and had  $[\alpha]_D -26.0^\circ$  in alcohol. It was finally purified by crystallisation from water containing 10 per cent. of

alcohol until the specific rotation of successive crops remained constant.

*l*-Hexylsuccinic acid separates from water or very dilute alcohol as a granular powder; it is freely soluble in the hot solvent, sparingly so in the cold, the solutions, however, showing a very pronounced tendency to supersaturation. It melts at 82–83°, whilst the racemic acid melts at 87°:

0.1302 gave 0.2840 CO<sub>2</sub> and 0.1035 H<sub>2</sub>O. C=59.5; H=8.8.

C<sub>10</sub>H<sub>18</sub>O<sub>4</sub> requires C=59.4; H=8.9 per cent.

The specific rotation was determined in the following solvents:

In ethyl-alcoholic solution:

$$l=2, c=4.0025, \alpha_D^{15.5} - 2.13^\circ, [\alpha]_D^{15.5} - 26.6^\circ.$$

In acetone solution:

$$l=2, c=1.4875, \alpha_D - 0.98^\circ, [\alpha]_D - 32.9^\circ.$$

In benzene solution:

$$l=2, c=1.8775, \alpha_D + 0.02^\circ, [\alpha]_D + 0.5^\circ.$$

Attempts to resolve *r*-hexylsuccinic acid by brucine or morphine in aqueous or alcoholic solution, or by strychnine in ethyl-alcoholic solution, were unsuccessful.

#### *Behaviour of the Active Hexylsuccinic Acids towards Alkali.*

Separate portions of the pure *l*-acid were heated under reflux on the water-bath with aqueous and aqueous-alcoholic (containing 10 per cent. of water) sodium hydroxide solution (1.183*N*; 20 c.c.) during five hours. The recovered acids had  $[\alpha]_D - 26.42^\circ$  and  $- 25.5^\circ$ , respectively, in ethyl-alcoholic solution; racemisation, therefore, did not occur in aqueous, and to only a very slight extent in alcoholic, solution, the slightly more marked effect of the latter reagent being in accordance with the recent observations of McKenzie and Wren (T., 1919, 115, 609) on the behaviour of *l*-mandelic acid under similar conditions.

*d*-Hexylsuccinic acid is markedly more stable under the combined influence of relatively high temperature and alkali hydroxide than is *d*-phenylsuccinic acid (Wren and Williams, *loc. cit.*). Thus, in an attempt to utilise some crude active acids, a specimen having  $[\alpha]_D + 13.0^\circ$  was heated with an excess of sodium hydroxide solution during five hours at 160°; the recovered acid had  $[\alpha]_D + 10.43^\circ$ , showing that racemisation had occurred to a comparatively slight extent, whilst under similar conditions, but with only two hours' heating, *d*-phenylsuccinic acid was almost completely racemised.

The authors desire to express their thanks to the Research Fund Committee of the Royal Society for a grant which has defrayed part of the cost of the investigation.

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### XXXIII.—*Surface Tension of Mixtures of Water and Alcohol.*

By JAMES BRIERLEY FIRTH.

A METHOD was required for conveniently determining small changes in concentration of the binary mixture, alcohol and water.

It appeared that a determination of the drop-number-concentration curve would provide a suitable method for this purpose, and it was with this object that the following experiments were carried out.

The utilisation of the drop-number-concentration curve as a means of analysis has been used successfully by Donnan and Barker (*Proc. Roy. Soc.*, 1911, [A], **85**, 557) and Lewis (*Phil. Mag.*, 1908, [vi], **15**, 499) for determining changes in concentration of dilute solutions.

The theory of the drop-pipette is that for a given size of opening the surface tension is directly proportional to the weight of the drop, and hence it may be used for determining relative surface tensions of solutions of different concentrations.

If  $V$  = total volume of the liquid used,

$n$  = total number of drops formed,

then the volume of each drop =  $\frac{V}{n}$ .

If  $\rho$  is the density of the liquid, then the weight of each drop =  $\frac{V\rho}{n}$ .

$\sigma$ , the surface tension, is proportional to the weight of the drop;

therefore  $\sigma = \kappa \frac{V\rho}{n}$

Similarly for another liquid:

$$\sigma_1 = \kappa \frac{V\rho_1}{n_1},$$

therefore

$$\frac{\sigma}{\sigma_1} = \frac{n_1 \rho}{n \rho_1},$$

$$\sigma = \frac{n_1}{n} \frac{\rho}{\rho_1} \sigma_1.$$

The principle assumes a static equilibrium, which is not correct, since the phenomenon is really dynamic, and in order to give an absolute measure of surface tension a small correction would be necessary (Guye and Perrot, *Arch. Sci. phys. nat.*, 1901, [iv], 11, 225; 1903, [iv], 15, 132; *J. Chim. physique*, 1917, 15, 164). This correction in utilising the drop-number-concentration curve as a means of analysis is unnecessary.

The drop-number for a constant volume will vary with the speed of dropping, since it takes an appreciable time for the freshly formed surface to attain equilibrium. It is essential, therefore, that the drops should form slowly, and that the rate of formation should remain as constant as possible throughout the series.

Duclaux (*Ann. Chim. Phys.*, 1878, [v], 13, 76) determined the surface tension of mixtures of alcohol and fatty acids with water by means of the drop-pipette, and showed that the surface-tension-concentration curve takes the form of a hyperbola, and the surface tension may be calculated from the equation:

$$\sigma = \kappa(\epsilon^x - 1),$$

where  $\sigma$  = surface tension, and  $x$  is the percentage concentration by weight.

#### EXPERIMENTAL.

The alcohol was dried over quicklime and distilled off, then dried with metallic calcium, and finally distilled, the first and last runnings being rejected.

The apparatus was similar to that used by Donnan and Barker (*loc. cit.*), the dropping tip being 3.5 mm. in diameter.

The experiments were carried out in an electrically-heated thermostat at 25°, and the rate of dropping was adjusted as near as possible to nine drops per minute.

The drop numbers of mixtures of alcohol and water were determined for mixtures containing from 2 to 96.5 per cent of water by volume. The drop numbers are the same concentration agreed to 1 in 500 drops.

#### Results.

The following table gives the measurements of drop numbers and surface tension, the surface tension being calculated from the equation:

$$\sigma = \frac{n_1}{n} \frac{\rho}{\rho_1} \sigma_1.$$

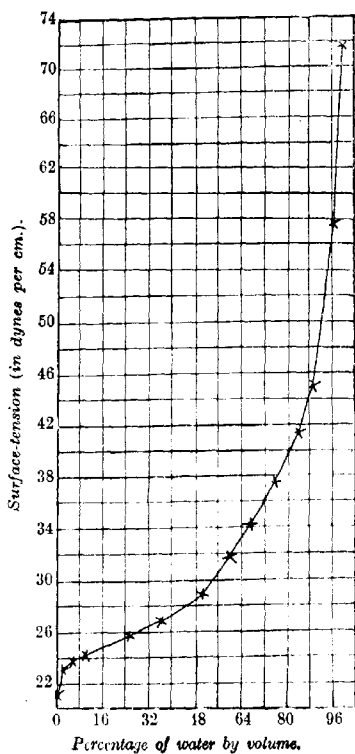
# 270 SURFACE TENSION OF MIXTURES OF WATER AND ALCOHOL.

The surface tension for water at 25° was taken as 71.78 dynes per cm.

TABLE I.

Percentage concentration of water by volume.	Drop number.	Surface tension in dynes/cm.	Percentage concentration of water by volume.	Drop number.	Surface tension in dynes/cm.
0	1826	21.30	60	1480	31.88
2	1710	23.13	67.3	1395	34.24
5	1708	23.73	75	1285	37.50
10	1714	24.14	84	1170	41.30
25	1690	25.76	89.2	1090	44.91
36.5	1675	26.83	96.5	854	57.72
50	1613	28.74	100	690	71.78

The surface-tension-concentration curve is shown in the figure  
The general results for binary mixtures have already been pub.



lished by various authors (compare Worley, T., 1914, 105, 260, 273), but as several important features have been revealed by the experiments it was thought desirable to record them.

There is a sudden fall in drop-number for 2 per cent. of water, then a further increase in the percentage of water up to 50 produces only a small change in drop-number; in fact, from 2 to 10 per cent. of water the drop-number is nearly constant. As the percentage of water increases beyond 50 the drop-number falls more rapidly with increased water content.

The results for the change in surface tension with concentration give a hyperbolic curve until a concentration of about 4 per cent. of water is reached, when the surface tension rapidly diminishes with diminution of water content.

It is interesting to note that the inflexion in the curve occurs at the point which practically corresponds with the concentration (4.4 per cent. of water) given by Young and Fortey (T., 1902, 81, 717) for a mixture of minimum boiling point.

The utility of the drop-number-concentration curve as a means of analysis varies with the range over which analysis is required.

Where the water content is more than 50 per cent. the curve may be used to give a fairly accurate analysis, but for concentrations below this the change in drop-number with concentration is not sufficiently great to give trustworthy results, whereas with the apparatus employed differences in concentration between 2 and 10 per cent. of water could not be detected with any degree of certainty.

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#### XXXIV.— $\beta\beta'$ -Dichloroethyl Sulphide.

By CHARLES STANLEY GIBSON and WILLIAM JACKSON POPE.

In the late autumn of 1917 we were requested by the Chemical Warfare Department to study the preparation of  $\beta\beta'$ -dichloroethyl sulphide,  $(\text{CH}_2\text{Cl}-\text{CH}_2)_2\text{S}$ , and in this connexion we thought it desirable to investigate carefully the interactions of ethylene and the two chlorides of sulphur. For obvious reasons, the results of this work remained unpublished, but as these reasons no longer exist, such of the information obtained as is of scientific interest

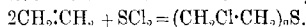


is now communicated. Since a number of workers in different countries were occupied with similar investigations, and their results, as reported, were often available for our information, we deal in the present paper only with our own work, and give the dates of the reports in which our results were communicated to the Government Department.

*Interaction of Ethylene and Sulphur Dichloride.*

The interaction of ethylene and sulphur dichloride was investigated by Guthrie some sixty years ago (*Quart. Journ. Chem. Soc.*, 1860, **12**, 116). He obtained a liquid product which possessed a vesicant action, and was doubtless a highly impure  $\beta\beta'$ -dichloroethyl sulphide; this observation was shortly afterwards confirmed by Niemann (*Annalen*, 1860, **116**, 288).

As the result of a number of preliminary experiments, we decided on the following as the most satisfactory method for preparing  $\beta\beta'$ -dichloroethyl sulphide by the direct addition of ethylene to sulphur dichloride, in accordance with the following equation:



Sulphur dichloride (50 grams), of the correct composition, free from iron and showing the specific gravity of 1.6227 at 17°, is introduced into a set of glass bulbs which can be rapidly shaken by mechanical means; a small quantity (0.5 gram) of finely powdered, highly absorbent charcoal which has been well dried by heating in a current of hydrogen is suspended in the sulphur dichloride. Ethylene, prepared by the action of ethyl alcohol vapour on heated phosphoric acid, as described by Newth (*T.*, 1901, **79**, 915), is freed from alcohol vapour by prolonged contact with water in a gasometer, and, after well drying by calcium chloride, is passed through the agitated sulphur dichloride, maintained at 40° to 45°, at such a rate that some escapes unabsorbed.

The ethylene is rapidly absorbed from the commencement, and the absorption ceases fairly suddenly when the reaction ends; owing to the volatility of sulphur dichloride, much of the latter is carried away by the excess of ethylene, and, in consequence, the quantity of ethylene absorbed is less than that indicated by the equation given above. The reaction proceeds similarly in the absence of charcoal, with the difference that absorption occurs much less rapidly in the latter stages and a smaller yield results. The temperature need not be rigidly limited; the reaction may be performed throughout at 50°, or may be started in the cold and allowed to warm up spontaneously or by externally applied heat to about 50°, but above this temperature unsatisfactory results are

obtained. Dilution of the sulphur dichloride with carbon tetrachloride has little effect on the yield or the purity of the product.

The liquid in the bulbs, which is of a straw-yellow colour, is now fractionally distilled under diminished pressure, and a fraction, boiling at  $134\text{--}137^\circ/50\text{ mm.}$ , is collected; this crystallises on cooling and melts at from  $5^\circ$  to  $9^\circ$ . This product is about 50 per cent. by weight of the sulphur dichloride treated, and contains approximately 90 per cent. by weight of  $\beta\beta'$ -dichloroethyl sulphide. On oxidation with nitric acid, it gives  $\beta\beta'$ -dichloroethyl sulphoxide, described below.

The above method for preparing  $\beta\beta'$ -dichloroethyl sulphide was described in a report to the Chemical Warfare Department dated January 16th, 1918; it gives a better yield and is more expeditious than the method devised by V. Meyer (*Ber.*, 1886, **19**, 3260) and perfected by Clarke (*T.*, 1912, **101**, 1583), which consists in converting (a) ethylene into ethylene chlorohydrin, (b) the latter into thiodiglycol by treatment with sodium sulphide, and (c) thiodiglycol into  $\beta\beta'$ -dichloroethyl sulphide by the action of hydrogen chloride. At the same time, the sulphur dichloride method is difficult to control, because  $\beta\beta'$ -dichloroethyl sulphide is acted on rapidly by sulphur dichloride; it is consequently necessary to work under such conditions that little or no sulphur dichloride remains long in contact with the  $\beta\beta'$ -dichloroethyl sulphide produced.

#### *Interaction of Ethylene and Sulphur Monochloride.*

On treating sulphur monochloride with ethylene at  $100^\circ$  and subjecting the liquid product to an elaborate method of purification, Guthrie (*Quart. Journ. Chem. Soc.*, 1861, **13**, 134) obtained a substance of slightly vesicant properties, to which he assigned the composition  $\text{C}_4\text{H}_2\text{Cl}_2\text{S}_2$ . Spring and Lecrenier (*Bull. Soc. chim.*, 1887, [ii], **48**, 629) showed that on oxidation with nitric acid this product yields  $\beta$ -chloroethylsulphonic acid, which is convertible into taurine,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ ; the same  $\beta$ -chloroethylsulphonic acid was obtained by James (*T.*, 1879, **35**, 806; 1885, **47**, 365) by the oxidation of  $\beta$ -chloroethyl thiocyanate. It is thus proved that Guthrie's compound is a disulphide of the constitution  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{S}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ . During the course of a recent discussion concerning the reaction between ethylene and sulphur monochloride (*J. Soc. Chem. Ind.*, 1919, **38**, 248r, 344r, 363r, 432r, and 463r), A. G. Green has contended that the interaction of ethylene and sulphur monochloride at  $30^\circ$  yields a product identical with that obtained by Guthrie at  $100^\circ$ , and suggests that this compound has the constitution  $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{S}_2\text{S}$ , but this formula is

the less probable in view of the experimental evidence adduced by Spring, Lecrenier, and James. On treating sulphur monochloride with ethylene at a variety of temperatures between  $70^{\circ}$  and the ordinary temperature, we have ourselves never obtained Guthrie's compound.

An exploratory examination of the interaction of ethylene and sulphur monochloride showed us that  $\beta\beta'$ -dichloroethyl sulphide is formed at all temperatures between the ordinary room temperature and about  $70^{\circ}$ . The following method was adopted as the best and most expeditious for the laboratory preparation of  $\beta\beta'$ -dichloroethyl sulphide.

Sulphur monochloride was purified by repeated distillation with small additions of sulphur from glass vessels; in order to ensure the absence of the dichloride, 2.5 per cent. of sulphur was dissolved in the purified product, which then had a density of 1.8862 at  $14.5^{\circ}$  and boiled at  $136.5$ – $137.5^{\circ}/760$  mm. About 5 per cent. by weight of  $\beta\beta'$ -dichloroethyl sulphide is added to the sulphur monochloride, which is then heated to  $55^{\circ}$  in the absorption bulbs and vigorously agitated while a rapid stream of ethylene, well dried by calcium chloride, is passed through the liquid. During the passage of the ethylene, heat is evolved, and the temperature should be maintained at  $60^{\circ}$  by cooling and heating when necessary; absorption begins immediately, and very quickly attains a uniform rate, stopping almost abruptly when two molecular proportions of ethylene have been absorbed by each one of sulphur monochloride present. Towards the latter part of the reaction, the liquid becomes turbid, owing to separation of sulphur in a viscous form, and when reaction is complete it is convenient to heat to  $100^{\circ}$  to produce a homogeneous solution, which can be readily poured out from the bulbs. On cooling the straw-coloured liquid, a copious deposit of crystalline sulphur separates; the crystallisation is facilitated by seeding. After remaining for some time in the cold, an almost colourless liquid may be decanted fairly completely from the compact, crystalline sulphur; this liquid crystallises on cooling and melts at  $9$ – $11^{\circ}$ . By distillation under diminished pressure, the liquid is found to consist of practically pure  $\beta\beta'$ -dichloroethyl sulphide containing about 3 per cent. of sulphur in solution. On distilling the hot liquid, before separation of the sulphur, under diminished pressure,  $\beta\beta'$ -dichloroethyl sulphide alone passes over, and, after sweeping residual vapour out of the distilling flask by a current of dry air, practically pure sulphur remains.

On cooling in ice-water, the distillate solidifies to a mass of colourless needles resembling glacial acetic acid in appearance, and melts, in general, at  $12$ – $12.5^{\circ}$ ; by repeated freezing, draining off

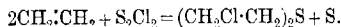
the residual liquid, melting, and again freezing, a product melting at  $13-13.5^\circ$  is obtained. This represents pure  $\beta\beta'$ -dichloroethyl sulphide, and was analysed, with the following results:

0.2616 gave 0.4725 AgCl. Cl=44.7.

0.2587 „ 0.3862 BaSO<sub>4</sub>. S=20.5.

C<sub>4</sub>H<sub>8</sub>Cl<sub>2</sub>S requires Cl=44.6; S=20.2 per cent.

During the course of a large number of preparations, carried out in general accordance with the conditions described above at temperatures between  $20^\circ$  and  $70^\circ$ , on quantities of about 40 grams of sulphur monochloride, it was established that the yield of pure  $\beta\beta'$ -dichloroethyl sulphide varied between 90 and 98 per cent. of that theoretically possible from the sulphur chloride. The sulphur remaining after the distillation retained a mere trace of resinous matter, and no product other than  $\beta\beta'$ -dichloroethyl sulphide distils; it is therefore concluded that the reaction represented by the appended equation proceeds quantitatively:



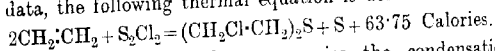
It should be observed that the reaction between ethylene and sulphur monochloride is accelerated by rise of temperature, absorption being about three times as rapid at  $60^\circ$  as at  $30^\circ$ . Whilst no reaction other than that indicated by the above equation is appreciable up to  $60^\circ$ , absorption commences normally at higher temperatures,  $80^\circ$  to  $85^\circ$ , but the liquid soon darkens and hydrogen chloride is evolved; absorption then does not proceed to the normal extent, and a very impure product is obtained. If the product of interaction at  $60^\circ$  is not heated to  $100^\circ$  before separation of the sulphur, it is observed that the latter is deposited in a gummy condition on cooling, and that the crystallisation is incomplete. This retention of the sulphur in some kind of "pseudo-solution" becomes more marked as the temperature of interaction is lowered. The  $\beta\beta'$ -dichloroethyl sulphide added to the sulphur monochloride before the reaction is started exercises some kind of catalytic influence in hastening the absorption; in its absence, absorption commences very slowly, and only attains the normal rate gradually, whilst with this initial addition absorption sets in immediately and proceeds at an appreciably uniform rate until the reaction is complete. After cessation of the absorption, no trace of sulphur monochloride can be detected in the product.

The reaction between ethylene and sulphur monochloride at  $60^\circ$  proceeds normally in the presence of metallic lead, but if metallic iron or an iron salt is present, the liquid darkens and hydrogen chloride is evolved; it is thus of importance to use sulphur chloride which is free from iron in order to avoid the well-known chlorin-

ating action exercised by sulphur monochloride in the presence of iron salts.

The method for the preparation of  $\beta\beta'$ -dichloroethyl sulphide from sulphur monochloride described above was communicated to the Chemical Warfare Department in reports dated January 30th and February 14th, 1918. In accordance with an agreement concerning the mutual exchange of information between the Allied Powers, these, together with the earlier report of January 16th, 1918, were immediately communicated to France and America. The information thus rendered available, first, that Guthrie's reaction between ethylene and sulphur dichloride is capable of giving a satisfactory yield of  $\beta\beta'$ -dichloroethyl sulphide, and, secondly, that a previously unsuspected reaction occurs between ethylene and sulphur monochloride, and results in a theoretical yield of  $\beta\beta'$ -dichloroethyl sulphide, was first passed between the Allies in these reports. The whole of the output of this toxic material achieved in Britain, France, and America during the recent war resulted from the application to large-scale production of the two reactions first shown to be economically possible in these three reports.

At the request of Sir Richard Threlfall, certain of the energy constants of  $\beta\beta'$ -dichloroethyl sulphide were determined in this laboratory by Messrs. C. T. Heycock and W. H. Mills. These gentlemen determined the heat of combustion of the liquid substance in the calorimetric bomb as 743.3 Calories at constant volume; the heat of formation from rhombic sulphur, amorphous carbon, and gaseous hydrogen and chlorine is thus calculated as +67.9 Calories. Messrs. Heycock and Atkinson also determined the heat of formation of sulphur monochloride from rhombic sulphur and gaseous chlorine as  $(2S, Cl_2) = +16.35$  Calories, and, in view of the uncertainty attaching to the published values for the heat of formation of ethylene, Messrs. Heycock and Mills made a new determination, using ethylene which had been carefully purified by liquefaction and distillation, which gave the value  $(2C, 2H_2) = -6.1$  Calories for amorphous carbon and gaseous hydrogen. From these data, the following thermal equation is derived:



The heat evolution which accompanies the condensation of ethylene with sulphur monochloride is thus a very large one, and requires careful consideration in connexion with large-scale preparations.

$\beta\beta'$ -Dichloroethyl sulphide has a density of 1.285 at  $15^\circ/4^\circ$ ; its refractive indices were determined by Mr. W. G. Palmer in this laboratory as 1.52776 for  $H_D$ , 1.53125 for  $N_D$ , and 1.53999 for

$H_v$  at  $15^\circ$ . The molecular depression of the freezing point by benzene was determined as  $54.6$ ; the latent heat of fusion is hence calculated as about 30 Calories.

Aluminium, lead, brass, iron, bronze, zinc, and tin are not acted on by  $\beta\beta'$ -dichloroethyl sulphide at the ordinary temperature; with the first three metals no appreciable action is noted at  $100^\circ$ , but the others named are attacked at this temperature, the action being most rapid in the case of tin. Titanic and stannic chlorides yield additive compounds with the substance. Sulphur dichloride acts vigorously on  $\beta\beta'$ -dichloroethyl sulphide at the ordinary temperature, but our preparations of sulphur monochloride do not attack the sulphide appreciably below about  $70^\circ$ ; above this temperature, reaction occurs, with evolution of hydrogen chloride and formation of more highly chlorinated derivatives of ethyl sulphide.

On treating  $\beta\beta'$ -dichloroethyl sulphide with concentrated nitric acid and gently warming, it is converted into  $\beta\beta'$ -dichloroethyl sulphoxide,  $(CH_2Cl \cdot CH_2)_2SO$ ; after diluting the solution and crystallising the precipitate from 50 per cent. alcohol, the sulphoxide is obtained in small, colourless plates melting at  $110^\circ$ :

0.2145 gave 0.3500 AgCl.  $Cl=40.4$ .

$C_4H_8OCl_2S$  requires  $Cl=40.5$  per cent.

The behaviour towards oxidising agents furnishes a ready method for distinguishing between Guthrie's disulphide and the monosulphide.

On adding bromine (2 mols.) to an ice-cold solution of  $\beta\beta'$ -dichloroethyl sulphide (1 mol.) in chloroform, a deep orange-coloured precipitate quickly separates; this, although it rapidly loses bromine, is sufficiently stable to allow of filtration, desiccation, and analysis. Two analyses of the product thus obtained showed the presence of 64.3 and 63.5 per cent. of bromine, whilst the compositions  $(CH_2Cl \cdot CH_2)_2S_2 \cdot 2Br_2$  and  $(CH_2Cl \cdot CH_2)_2S \cdot Br_2$  require 66.8 and 50.2 per cent. of bromine respectively. On keeping the dried, orange-coloured substance, it becomes converted, with loss of bromine, into a bright yellow solid melting at  $43-44^\circ$ ; this substance could not be further purified, owing to its instability, but was found to contain 48.5 per cent. of bromine and to yield the sulphoxide,  $(CH_2Cl \cdot CH_2)_2SO$ , melting at  $110^\circ$ , on treatment with dilute sodium hydroxide solution.

It is thus indicated that the yellow compound melting at  $43-44^\circ$  is the dibromide of  $\beta\beta'$ -dichloroethyl sulphide, corresponding with the sulphoxide, and that the orange-coloured substance is the *tribromide*.

Our thanks are due to Mr. G. M. Bennett, M.A., for valuable

assistance in connexion with the experimental work described in the present paper.

This paper is published with the concurrence of the Government Department concerned.

THE CHEMICAL LABORATORY,

UNIVERSITY OF CAMBRIDGE.

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### XXXV.—*The Action of Ethyl Chloroformate on Pyridine and Quinoline.*

By THOMAS HOPKINS.

COMPARATIVELY few experiments appear to have been carried out on the action of halogen derivatives of the simpler aliphatic esters or the somewhat closely related compounds, the acid chlorides, on pyridine and quinoline. The first investigations were those of Gerichten (*Ber.*, 1882, **15**, 1251) and Krüger (*Ber.*, 1890, **23**, 2608), who obtained pyridine-betaine hydrochloride by the interaction of chloroacetic acid and pyridine. It was found that at 202–205°, pyridine-betaine hydrochloride decomposes into pyridine, methyl chloride, and carbon dioxide. Below this temperature, however, pyridine-betaine appears to be quite stable. Rhoussopoulos (*Ber.*, 1882, **15**, 2006) treated quinoline with ethyl chloroacetate, and obtained the chloride of quinoline-betaine ethyl ester. Dennstedt and Zimmermann (*Ber.*, 1886, **19**, 75) studied the interaction of pyridine and acetyl chloride. They found that an additive product was first formed, and, on heating over the water-bath, the first products isolated were pyridine and dehydracetic acid. The latter is formed from the acetyl chloride, and the pyridine is regarded as acting by removing the elements of hydrogen chloride.

The final products of these reactions are colourless substances. With ethyl chloroformate, pyridine forms a colourless, additive compound, which rapidly changes to red. The additive compounds of pyridine with hydrogen chloride, methyl chloride, or benzyl chloride are all colourless substances. It does not appear possible to put forward any structural explanation of the intense colour of the compound formed from ethyl chloroformate and pyridine without recourse to the hypothesis of partial valency. As at present such an hypothesis does not admit of experimental verification, the cause of the colour has not been satisfactorily elucidated. The compound of quinoline and ethyl chloroformate is canary-yellow and is only stable at very low temperatures.

This reaction is interesting in two other respects. First, it furnishes a means for producing ethyl chloride, the ease of decomposition of the pyridine compound in the absence of moisture leading to the view that the pyridine may assume the rôle of a catalyst. Secondly, the interaction of pyridine and ethyl chloroformate may be utilised for detecting small quantities of pyridine in commercial ammonium nitrate. The pyridine is first extracted with about 30 c.c. of chloroform, and then one or two drops of ethyl chloroformate are added. The presence of pyridine is indicated by the appearance of a red tint.

#### EXPERIMENTAL.

##### *Ethyl Chloroformate and Pyridine.*

In a preliminary experiment, 79 grams of pyridine (1 mol.) and 108 grams of ethyl chloroformate (1 mol.) were used. The pyridine was placed in a round-bottomed flask, which was surrounded by a freezing mixture. The flask was attached to a reflux condenser, and the ethyl chloroformate added very slowly from a dropping funnel. The condenser was connected to two coiled receivers immersed in a freezing mixture, thence to a tube with lime-water, and finally to a tube containing bromine water. During the addition, a vigorous reaction took place, and the lime-water rapidly became milky, a strong stream of gas with a very sweet, ethereal odour issuing from the exit tube. When the addition of the ethyl chloroformate was complete, a dark red paste was formed in the flask. The contents of the latter were raised to boiling point, and a strong evolution of gas occurred during this process. The apparatus was then detached and the contents of the flask and the coiled receivers were examined. The liquid condensed in the coiled receivers was proved by analysis to be ethyl chloride. The contents of the flask consisted of a dark red oil and a black, viscous mass. The greater part of the oil distilled at 115—120°, and was pyridine. It contained also a white, amorphous solid, which distilled at about 230°. The same white substance was isolated from the black, viscous mass by solution in alcohol and crystallisation in a vacuum. It contained Cl=28.89, whilst pyridine hydrochloride requires Cl=30.73 per cent. The substance was soluble in water, and when the solution was rendered alkaline with sodium hydroxide and saturated with salt, pyridine separated. This experiment led to the conclusion that the products of decomposition of the reaction were ethyl chloride, carbon dioxide, pyridine, and pyridine hydrochloride.

In order to control the intensity of the reaction, xylene and ether were used as diluents, but in each case when either the ethyl chloro-



formate was added to the pyridine or vice versa, the reaction appeared to be equally vigorous. The same intense reaction was observed when the reagents were kept at  $-10^{\circ}$  during the addition.

*The Influence of Moisture on the Reaction.*—About 200 grams of pyridine distilling at  $115-120^{\circ}$  were twice fractionated over solid potassium hydroxide, and the portion distilling at  $115^{\circ}$  was collected separately and allowed to remain over sodium overnight. Gas bubbles were evolved, showing that moisture was present. Sodium wire was unsuitable, for it charred the pyridine completely.

The ethyl chloroformate was fractionated, and the portion distilling at  $93^{\circ}$  separately collected. Any free acid was first destroyed by adding a little calcium carbonate. This fraction was also allowed to remain over sodium for several days and re-distilled.

With these purified materials, the interaction between gram-molecular proportions of the two substances was studied in a desiccator containing sulphuric acid, which itself was kept cold by a freezing mixture. The pyridine was dissolved in 200 c.c. of dry ether contained in a wide-mouthed bottle. Through the opening in the lid of the desiccator a dropping funnel was fixed, the stem of which was drawn out into a capillary tube terminating about 2 cm. above the surface of the liquid in the bottle. The ethyl chloroformate was placed in the dropping funnel, which was then closed with a calcium chloride tube. To the side-tube of the desiccator two calcium chloride tubes in series were fixed. After twenty-four hours, the tap of the side-tube was adjusted to admit such an amount of dried air as would allow the ethyl chloroformate to enter at the rate of a drop per second.

The same colour changes took place as in the preliminary experiments, and effervescence set in when the addition became too rapid. The dark red product was thoroughly washed six times with fresh quantities of dry ether and kept in a vacuum overnight. Next morning the surface layer was white, owing to the vacuum not having been maintained. The layer was removed, and the rest of the mass showed a uniform rose-red colour. The nature of this product was then examined.

(1) The percentage of chlorine in it was estimated by the Carius method. Some difficulty was experienced in this, because the product was so sensitive to traces of moisture. Owing to the ease with which the substance decomposes when exposed for a short time to the atmosphere, several estimations had to be carried out before satisfactory results were obtained. When the operation of weighing and transferring to the tube was done expeditiously, the percentage of chlorine was found to vary from 19.2 to 19.46, whilst  $C_8H_{10}O_2NCl$  requires  $Cl=18.93$  per cent.

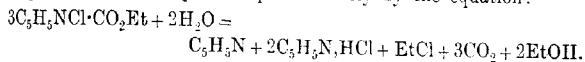
(2) The red substance when exposed to the atmosphere quickly effervesced, thus showing that decomposition was taking place. Water decomposed it rapidly with a strong evolution of carbon dioxide and ethyl chloride.

(3) *Hydrolytic Decomposition.*—The compound (19.3 grams) was placed in a small flask attached to a reflux condenser, and about 50 c.c. of water were added down the condenser tube, when a vigorous decomposition took place. When the evolution of gas had slackened, the contents of the flask were kept gently boiling for one hour. The aqueous solution was clear but slightly yellow, and had a strong odour of pyridine. The aqueous solution was then distilled, and two fractions were obtained, namely, an aqueous distillate up to 150°, and a white sublimate which appeared to distil at about 220°.

The aqueous distillate was strongly alkaline with a strong odour of pyridine, and the sulphuric acid-dichromate test showed conclusively the presence of alcohol.

The weight of white solid recovered was approximately 40 per cent. of the original weight taken. It was readily soluble in water or alcohol, giving colourless solutions, but insoluble in ether. It was recrystallised from water, dried in a vacuum for two days, and finally washed six times with dry ether. It melted at 120–122° and distilled unchanged at 220°. Analysis showed it to consist of pyridine hydrochloride (Found: Cl=30.09.  $C_5H_5N, HCl$  requires Cl=30.73 per cent.).

It is evident that the products of hydrolytic decomposition are free pyridine, alcohol, carbon dioxide, ethyl chloride, and pyridine hydrochloride to the extent of about 40 per cent. This change may therefore be expressed quantitatively by the equation:



#### *Ethyl Chloroformate and Quinoline.*

Experiments were carried out on the interaction of quinoline (b. p. 134–140°) and ethyl chloroformate in a manner analogous to that described above. A yellow, amorphous solid was formed, which was far more stable than the corresponding pyridine compound. It could be submitted to the atmosphere for a considerable time without decomposition. On heating at 100°, it decomposed into quinoline, carbon dioxide, ethyl chloride, and quinoline hydrochloride, although this decomposition is slower than in the case of the pyridine compound. Water decomposes the quinoline compound in a like manner to the pyridine compound. The

chlorine content of the substance was determined by the Carius method, and the results varied from 14.25 to 14.95, whilst  $C_{12}H_{13}O_2NCl$  requires  $Cl=14.92$  per cent. The variation in the results may be caused by the quality of the quinoline employed, which was isolated by fractionating the technical product. Pure quinoline distilling exactly at  $239^\circ$  was obtained, and the experiments were repeated. The ethyl chloroformate had been specially purified. It was found, however, that the pure quinoline did not react with ethyl chloroformate at the ordinary temperature, at zero, or at  $-10^\circ$ . They interacted only at the temperature of solid carbon dioxide, and formed a canary-coloured product, as in the preliminary experiments. When the yellow compound is removed from the solid carbon dioxide and allowed to remain at the ordinary temperature, it quickly liquefies and decomposes. The decomposition is brisk, and carbon dioxide and ethyl chloride are evolved. The extent to which this decomposition takes place was then investigated. In a test-tube 10 cm. long provided with a side-tube and stopcock was placed 0.32 gram of quinoline. The tube was closed with an air-tight stopper carrying a short tube with a stopcock. This served the purpose of displacing the air with dry carbon dioxide at the initial stage and sweeping out any ethyl chloride into a Lunge nitrometer. The tube was placed in solid carbon dioxide in a Dewar vessel, and the equivalent of ethyl chloroformate added drop by drop. Particular care was taken to avoid access of moisture, and the tube and its contents were allowed to remain in the solid carbon dioxide for five hours. It was then connected with the nitrometer, the tube allowed to remain in the air, and the issuing ethyl chloride collected over 30 per cent. potassium hydroxide. By this experiment, 24.8 per cent. of the available ethyl chloride was accounted for (theoretical, 27.16 per cent.). The residue contained the hydrochloride, which explains the discrepancy. The reaction is very sensitive to moisture, and it was found that where no precautions were taken to eliminate moisture, 23.3 per cent. of hydrochloride is formed in the decomposition, and the available ethyl chloride is much lessened.

The author is indebted to the Research Committee of Messrs. Nobel's Explosives Co., Ltd., and particularly to Mr. Rintoul, for the facilities accorded him in carrying out this investigation. He is also indebted to Messrs. Nolan and Hepworth for friendly criticism of the experiments.

THE RESEARCH LABORATORIES,  
STEVENSTON.

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XXXVI.—*The Action of Nitric Acid on Unsaturated Hydrocarbons. The Action of Nitric Acid on Acetylene.*

By KENNEDY JOSEPH PREVITÉ ORTON and PHYLLIS VIOLET MCKIE.

THE action of nitric acid, in contrast to nitrogen peroxide, on unsaturated (non-aromatic) hydrocarbons has not yet been thoroughly examined. Such references as are found in the literature indicate that complete oxidation to oxalic acid or carbon dioxide usually occurs. Baschieri (*Atti R. Accad. Lincei*, 1901, [v], **9**, i, 391) and Testoni and Mascarelli (*ibid.*, 1902, [v], **10**, i, 442; *Gazzetta*, 1903, **33**, ii, 319), on examining the action of fuming nitric acid on acetylene, obtained, however, a mixture of complex substances, the constitution and even the composition of which were not with certainty elucidated. J. Schmidt (*Ber.*, 1901, **34**, 619), who prepared from stilbene and nitrogen dioxide a dinitrostilbene, suggested that this behaviour foreshadows the manner of reaction with acetylene.

We have examined the interaction of nitric acid and acetylene under varying conditions of concentration, of temperature, and in the presence of metallic salts, in the first instance to ascertain whether tetranitromethane or substances such as nitroform, which could be easily converted into tetranitromethane by nitration, were produced. This quest has been highly successful, and thus a source of tetranitromethane, which has a certain usefulness as a high explosive, from inexpensive materials has been obtained.

Acetylene is absorbed with very great ease by absolute nitric acid, or by mixtures of nitric acid and sulphuric acid. With dilution of the nitric acid, the rate of interaction, and hence the readiness of the absorption, decreases. Rise of temperature and the presence of the catalyst (mercury salt) cause an increase in the rate of the interaction and readiness of absorption. In these comparative statements of the readiness of absorption, it is to be understood that the method of bringing the gas and the liquid into contact is unchanged. Obviously intimate intermingling of a gas and a liquid will promote absorption and interaction, and may lead to as ready an absorption by a dilute acid at low temperature as is with less efficient mixing only found at more favourable temperatures and concentrations of the acid.

The reaction is accompanied by a small development of heat. On the scale of our experiments, the temperature was kept thereby at 5--8° above the laboratory temperature.

The products of the interaction of acetylene and nitric acid are various; and the nature and the proportion of these products is largely determined by the concentration of the acid, by the temperature, and by the presence of a catalyst or of sulphuric acid.

The Italian investigators (*loc. cit.*) isolated from the interaction of acetylene and nitric acid (D 1.52; the proportions are not stated) at low temperatures small quantities of different solid products, some neutral and some acid, which were frequently explosive. Nitroform was also found among the products.

Omitting the products of reduction of nitric acid, the reaction yields nitroform and certain substances, which can be converted into tetranitromethane, carbon dioxide (and a trace of carbon monoxide), and other substances--among them sometimes oxalic acid ("O.S." in the tables)--which cannot be converted into tetranitromethane; the latter may predominate in certain circumstances, such as high or low concentration of the nitric acid or low temperature. Of the antecedents of tetranitromethane, nitroform usually amounts to about 75--85 per cent., and the others to about 15 per cent. Of the metals which we have tried as catalysts, only mercury causes a marked increase of the proportion of nitroform, etc., and at the same time reduces to a very small proportion the by-products which do not yield tetranitromethane. In fact, the reaction is simplified, and the acetylene is quantitatively represented by nitroform, etc., and carbon dioxide. Table I summarises the results of experiments, which illustrate the effect of concentration of acid, temperature, presence of mercury nitrate, or of sulphuric acid.

Under "t.n.m." in the table is the quantity of tetranitromethane (as a percentage of the acetylene reacting) which can be obtained from the product by a treatment described later. This quantity is a convenient measure of the extent to which nitroform and the other antecedents are produced under given conditions. If 2 moles of tetranitromethane were formed from one of acetylene, "t.n.m." would amount to 1508 per cent. in a quantitative yield, or if 1 mole of acetylene yields one of tetranitromethane, which is far more probable, 754 per cent.

TABLE I.

*A. Varying Concentration of Nitric Acid. Temperature, 15°.*

Experi- ment.	Percentage of nitric acid.	C <sub>2</sub> H <sub>2</sub> absorbed by 100 grams of nitric acid. Litres.	"t.n.m." as per- centage of C <sub>2</sub> H <sub>2</sub> absorbed.
1.....	100.0	1.610	75.5
2.....	97.5	1.516	103.0
3.....	95.0	1.296	238.0
4.....	90.0	1.097	160.0
5.....	85.0	0.546	158.0
6.....	70.0	1.043	37.4

*B. Sulphuric Acid present. Temperature, 15°.*

Experi- ment.	H <sub>2</sub> SO <sub>4</sub> / HNO <sub>3</sub> .	C <sub>2</sub> H <sub>2</sub> ab- sorbed per 100 grams of nitric acid. Litres.	CO <sub>2</sub> evolved per 100 grams of nitric acid. Litres.	CO <sub>2</sub> /C <sub>2</sub> H <sub>2</sub> by vol- ume.	"t.n.m." as percent- age of C <sub>2</sub> H <sub>2</sub> ab- sorbed.	"O.S." as a percent- age.
7.....	0.11/1	1.336	0.295	0.25/1	148.5	77.9
8.....	0.5 /1	1.41	0.137	0.09/1	0.0	95.6
9.....	0.5 /1	1.615	1.092	0.67/1	129.0	57.8
10.....	2.6 /1	1.774	0.17	0.1 /1	0.0	95.9

In Experiment 9, 0.33 per cent. of mercuric nitrate was present.  
In Experiments 6 and 10 the temperature was 30°.

*C. Mercuric Nitrate present, 0.66 per cent. Temperature, 15°.*

Experi- ment.	Percentage of nitric acid.	C <sub>2</sub> H <sub>2</sub> ab- sorbed by 100 grams of nitric acid. Litres.	CO <sub>2</sub> evolved per 100 grams of nitric acid. Litres.	CO <sub>2</sub> /C <sub>2</sub> H <sub>2</sub> by vol- ume.	"t.n.m." as percent- age of C <sub>2</sub> H <sub>2</sub> .	"O.S." as a percent- age.
11.....	90	1.490	2.27	1.52/1	204	9.82

*D. Temperature Varied.*

	T°.					
12...	-3°	95	1.20	0.54	0.394/1	104
13...	15	95	1.296	1.04	0.8 /1	238
14...	30	95	1.49	1.565	1.05/1	331
						61.0
						44.0
						25.4

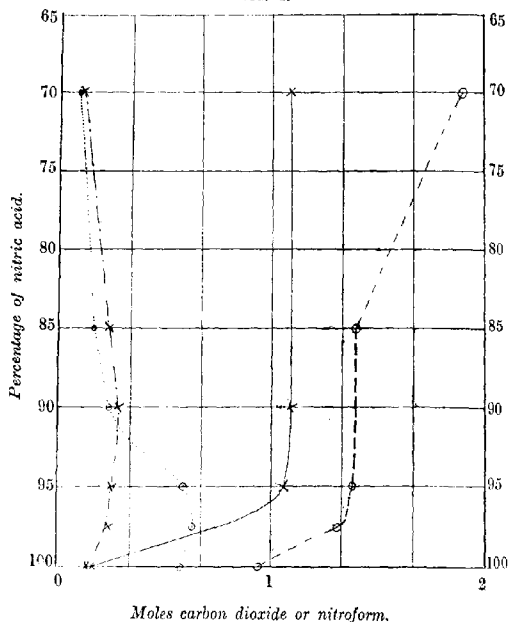
*E. Mercuric Nitrate, 0.3—0.66 per cent. Temperature, 30°.*

15.....	95	1.571	2.22	1.41/1	523	0.0
16.....	100	3.456	4.87	1.4 /1	410	2.4
17.....	70	0.581	1.1	1.91/1	47	1.9

It will be seen that both a high concentration (in the absence of mercury salt) and a low concentration of nitric acid are unfavourable to the formation of nitroform and the other antecedents of

tetranitromethane. The optimum concentration is about 95–97 per cent. Obviously in the interaction of nitric acid and acetylene the acid becomes diluted, and the yield will only be a maximum when a small quantity of acetylene is absorbed by this acid (Expt. 15). To obtain the maximum quantity of nitroform (and tetranitromethane) in one operation the absorption of 3.5–3.7 litres of

FIG. 1.



acetylene by 100 grams of "100 per cent." nitric acid, to which 0.33 gram of mercury nitrate has been added, is best (Expt. 16). The yield of nitroform is then about 14.2 grams, and of tetranitromethane 16.7 grams (or 410 per cent.). At the lower concentrations (70 per cent.) of nitric acid, oxidation to carbon dioxide increases, the ratio  $\text{CO}_2 : \text{C}_2\text{H}_2$  (by volume, molar) approaches and in Expt. 17, under the influence of mercury nitrate, nearly

reaches 2 : 1. The dependence of the products of the reaction on the concentration of the nitric acid is well shown in Fig. 1. This indicates first the volume of carbon dioxide for one volume of acetylene, plotted against the concentration of nitric acid, (a) when no mercury salt has been added, (b) when mercury salt is present, and secondly the moles of nitroform for one mole of acetylene under similar different conditions; about 1 litre of acetylene has reacted with 100 grams of nitric acid.

*Effect of the Presence of Various Metallic Salts.*

The effect of the presence of small quantities of salts of platinum, silver, uranium, copper, and mercury on the reaction between nitric acid and acetylene has been examined. The metals were added as nitrates, except platinum, which was in the form of chloroplatinic acid. The quantities used were molar equivalents of the amount of the mercury nitrate required to form a 0.33 per cent. solution. In 95 per cent. nitric acid solution was complete, or nearly complete, except with platinum, when a heavy, yellow precipitate appeared and remained throughout. With copper a precipitate appeared during the reaction. Table II summarises the results. The nitric acid was diluted to 95 per cent., and the temperature was 30°.

TABLE II.

Experi- ment.	Metal.	C <sub>2</sub> H <sub>2</sub> absorbed by 100 grams of nitric acid. Litres.	CO <sub>2</sub> evolved per 100 grams of nitric acid. Litres.	" t.n.m." as a per- centage of C <sub>2</sub> H <sub>2</sub> .	Percent- age of C in C <sub>2</sub> H <sub>2</sub> becoming " t.n.m."	Percent- age of C in C <sub>2</sub> H <sub>2</sub> becoming CO <sub>2</sub> .	Percent- age of C in C <sub>2</sub> H <sub>2</sub> becoming " O.N."
18 .....	Pt	2.68	2.25	203	13.5	41.8	44.7
19 .....	Ag	2.73	2.20	221	14.7	49.3	36.0
20 .....	Ur	2.60	3.32	222	14.9	63.6	21.5
21 .....	Cu	2.55	2.64	371	24.2	51.5	24.3
22 .....	Hg	3.02	4.38	453	29.18	70.81	0.0
23 .....	None	2.81	2.72	341	22.6	49.0	28.4

Mercury stands alone in having a markedly favourable effect on the rate of interaction, and hence on the readiness of absorption. Again, mercury is the only metal of those examined which exerts a beneficial influence on the production of nitroform and hence tetranitromethane. All the metals, save copper, favour oxidation of the acetylene, at the expense of the production of nitroform, etc.; uranium is peculiarly active in this respect. The experiment in which mercury is present stands out in that "other substances" are absent. Platinum has the opposite effect, and causes an increase in the proportion of by-products.



The proportion of mercury is important; the most favourable proportion lies below 1 per cent. Table III summarizes the results of experiments made with the object of ascertaining exactly the best proportion, which is obviously 0.3–0.4 per cent.

TABLE III.

Temperature, 30°.

Ex-	Per-		C <sub>2</sub> H <sub>2</sub> ab-	CO <sub>2</sub>		Percent-	Percent-	Percent-
peri-	cent-		sorbed	evolved		age	age	age
ment.	age		by 100	per 100	"t.n.m."	of C in	of C in	of C in
acid.	of Hg(NO <sub>3</sub> ) <sub>2</sub>	grams	grams	grams	as a per-	C <sub>2</sub> H <sub>2</sub> be-	C <sub>2</sub> H <sub>2</sub> be-	C <sub>2</sub> H <sub>2</sub> be-
centage.	centage.	acid.	of nitric	of nitric	centage	coming	coming	coming
		Litres.	Litres.	Litres.	of C <sub>2</sub> H <sub>2</sub> .	"t.n.m."	CO <sub>2</sub> .	"O.S."
24.....	95.0	0.66	3.06	4.39	383	25.4	71.5	3.1
25.....	95.0	0.33	3.02	4.38	453	29.2	70.8	0.0
26.....	95.0	0.33	1.55	1.62	552	37.1	62.7	0.2
27.....	97.5	0.28	3.16	4.34	429	28.5	68.2	3.3
28.....	95.0	0.165	3.03	3.83	431	28.6	63.1	8.2
29.....	95.0	0.0	2.81	2.72	341	22.6	49.0	28.4

The mercury salt appears to have more than one effect on the interaction of acetylene and nitric acid, and at different concentrations as well as at different temperatures one or other of these effects may be the more marked.

The most characteristic effect is the elimination of products other than the precursors of tetranitromethane or carbon dioxide. These products have been grouped together under "other substances," but two important groups can be distinguished. In the first place, when the nitric acid is highly concentrated, substances are produced in considerable quantity which do not on further treatment—"nitration"—yield tetranitromethane. These are probably the substances isolated by Mascarelli and his co-workers. Thus we find that with 100 per cent. nitric acid at 14° "O.S." may represent 86 per cent. of the acetylene absorbed, but in the presence of a mercury salt at 30° "O.S." is reduced to zero. The large increase in the yield of tetranitromethane from less than 100 per cent. in the first experiment to 460 per cent. in the second shows that the effect of a mercury salt is to cause the substitution of precursors of tetranitromethane for these other substances.

In less concentrated nitric acid, about 95 per cent., another effect becomes apparent. Now in the absence of mercury an important by-product is oxalic acid [Ca(CO<sub>2</sub>)<sub>2</sub>, H<sub>2</sub>O gave CaCO<sub>3</sub> = 69.15. Calc., CaCO<sub>3</sub> = 68.50 per cent.], which can be readily isolated from or estimated in the product. When 1.5 litres of acetylene are absorbed by 100 grams of nitric acid (95 per cent. at 30°), as much as 25 per cent. of the acetylene appears as oxalic acid. If a mercury salt is

present, however, only a very small quantity of oxalic acid is found, and there is a correspondingly large increase in the carbon dioxide. Direct experiment shows that a mercury salt does not cause the oxidation of oxalic acid by nitric acid, and it seems probable, therefore, that now, in the presence of mercury salt, some intermediary other than oxalic acid is directly oxidised to carbon dioxide.

The presence of a mercury salt also modifies the reaction of acetylene with a mixture of nitric acid and sulphuric acid. A comparison of experiments 8 and 9 (table I) demonstrates this effect. It will be seen that the precursors of tetranitromethane are only produced in the presence of a mercury salt, and, further, that concurrently there is more oxidation of the acetylene.

The mercury salt is without effect on the conversion of primary products of the interaction of acetylene and nitric acid into tetranitromethane, for addition after the absorption of the acetylene does not affect the yield of tetranitromethane in the subsequent treatment. The mercury salt then determines only the course of the primary interaction.

*Formation of Nitroform and other Precursors of Tetranitromethane.*—In order to account for the formation of tetranitromethane in the interaction of diacetylorthonitric acid, acetyl nitrate or nitric acid and acetic anhydride, Pictet and Genequand (*Ber.*, 1903, 36, 2225) suggested that nitroform, which they isolated, or even trinitroacetic acid, precedes tetranitromethane. The formation of tetranitromethane by the nitration of nitroform had earlier been demonstrated by Schischkov (*Annalen*, 1861, 119, 248), who used a mixture of nitric and sulphuric acids.

Nitroform, as its characteristic ammonium salt, can easily be isolated from the product. The estimation in the complex acid mixture is not so simple; but after removal of the "nitrous acid" by ammonium nitrate the nitroform can be distilled in a current of steam or extracted with ether, and then titrated in the distillate or extract with alkali hydroxide, or, better, with permanganate.

The quantity of nitroform thus determined does not represent more than 85—87 per cent. of the tetranitromethane which can be obtained from the product, and is in some circumstances less. No want of accuracy which can be detected in the method of estimation of the nitroform will account for this discrepancy between the quantities of nitroform and tetranitromethane.

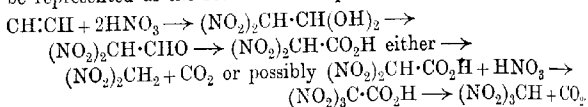
Clear evidence that the product contains substances other than nitroform which yield tetranitromethane when heated with sulphuric acid is adduced by the following experiment. The product was obtained by passing acetylene into 95 per cent. nitric acid at

30°, 0.33 per cent. of mercuric nitrate being present. The nitroform found in a portion of the fresh product was equivalent to 15.6 grams of tetranitromethane, whereas the product yielded 20 grams. An equal portion of the product was heated at 85° for two hours before treatment with sulphuric acid. The yield of tetranitromethane in this portion was now 16.6 grams, and the nitroform therein was equivalent to 15.3 grams.

The yield of tetranitromethane also falls off, rapidly at first, if the product is kept for some time at the ordinary temperature, whereas the decomposition of nitroform in the product, which is also observed, is very much slower.

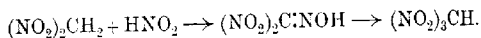
Obviously substances which can yield tetranitromethane have been destroyed by heating or keeping the product. It is clear that they have not been converted into nitroform, for the quantity of nitroform is approximately unchanged and, it is to be noted, after the heating, is nearly equivalent to the tetranitromethane.

The formation of nitroform from acetylene and nitric acid can be represented as the result of a simple addition:



(The addition of nitrogen peroxide is not considered.)

Dinitromethane very readily reacts with nitrous acid (Duden, *Ber.*, 1893, **26**, 3003), yielding the *isonitroso*-compound, which under the conditions would probably be oxidised to nitroform, thus:



The *isonitroso*-compound does not appear usually to be present in the product, for in normal experiments there is no marked indication of the blood-red colour which it yields with alkalis (Duden, *loc. cit.*). At lower dilutions of nitric acid, however, this reaction is obvious on rendering the product alkaline.

When nitroform is produced by the routes indicated above, one mole of acetylene yields one mole of nitroform and one mole of carbon dioxide; hence as a maximum only 50 per cent. of the carbon of the acetylene would become nitroform.

#### EXPERIMENTAL.

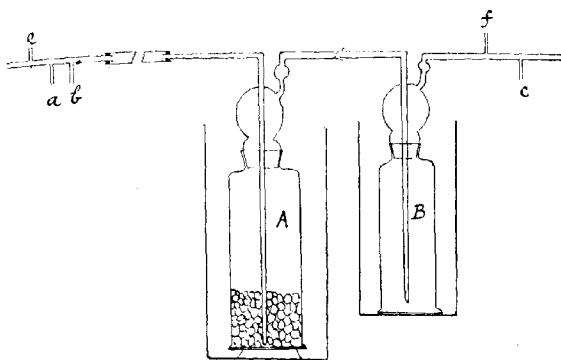
The essential parts of the apparatus are shown in Fig. 2. Acetylene is absorbed so readily, at least by sufficiently concentrated nitric acid at moderate temperatures, that the Drechsel bubbler (4), in which the end of the inlet tube is somewhat con-

stricted, serves as the reaction vessel; the bubbles of gas are broken by a layer of glass beads. This bubbler, which is nearly full, is immersed in a bath maintained at a constant temperature, usually 30°.

The second bubbler (*B*), which is placed in a cooling-bath, contains 30 c.c. of sulphuric acid (96—97 per cent.); all the oxides of nitrogen coming from (*A*) are absorbed in (*B*). No nitrous or nitric oxides have been found in the gas, which passes through the sulphuric acid. Safety devices for meeting a development of negative pressure or a sudden positive pressure are placed at *a*, *b*, and *c*. Samples of gas for analysis can be drawn off from the pipe line at *e* and *f*.

The acetylene, which was not purified, was dried by calcium

FIG. 2.



chloride. In this apparatus, good absorption (more than 90 per cent. under the best conditions) was obtained up to a speed of 400 c.c. per hour. Usually the speed was considerably less, about 150—200 c.c. per hour.

The nitric acid was prepared from a crude, fuming nitric acid ( $D_{15} 1.5$ ), which contained much iodine as iodic acid, by distilling from an equal weight of sulphuric acid. The distillate had  $D_{15} 1.545$ ; the acid contained 2.2 per cent. of "nitrous acid," as determined by potassium permanganate.

Mercuric nitrate (0.5 gram:0.33 per cent.) is placed in the bubbler, then water (7.5 c.c. when a 95 per cent. nitric acid is used), and finally the nitric acid (138.6 grams=90 c.c.). The mercuric nitrate dissolves completely; the quantity of 95 per cent. nitric acid just given will dissolve 1.2—1.3 grams at the ordinary

temperature. Absolute nitric acid dissolves very little mercuric nitrate which, at the beginning of the experiment, is in suspension, but dissolves later.

It is not advantageous to pass more than 4.5–4.6 litres of acetylene into A, although when absolute nitric acid is used this may be increased to 5 litres. As the reaction proceeds, the nitric acid is diluted; not only is the reaction then more tardy, and hence the absorption poorer, but oxidation of the acetylene, and hence the evolution of carbon dioxide, becomes more prominent. At the early stages of the reaction, very little gas leaves (A); later, oxides of nitrogen and carbon dioxide are evolved, towards the end of the experiment vigorously.

The results of typical experiments are summarised in table IV.

TABLE IV.

In all experiments, 0.33 per cent. of mercury nitrate was present.

Ex- peri- ment.	Per- cent. age of nitric acid.	$C_2H_2$ absorbed by 100 grams of nitric acid. Litres.	Nitro- form. Grams.	$CO_2$ evolved by 100 grams of nitric acid. Litres.	"t.n.m." of $C_2H_2$ as a per- centage of $C_2H_2$ .	Percent- age of C in $C_2H_2$ be- coming "t.n.m."	Percent- age of C in $C_2H_2$ be- coming "O.S."	Percent- age of C in $C_2H_2$ be- coming "O.S."
30.....	95.0	3.068	10.3	4.38	436	28.94	71.04	0.0
31.....	97.5	3.163	10.5	4.34	430	28.8	68.5	2.3
32.....	100.0	3.456	11.0	4.87	410	27.6	70.5	2.4
33.....	100.0	2.883	9.9	4.07	448	29.73	70.3	0.0

*Preparation of Nitroform.*—The product is diluted 1 to 10, and then the nitrous acid removed by ammonium nitrate, 20 grams to 100 c.c. of the diluted product. The nitroform is then extracted by ether, preferably in a continuous apparatus. The ethereal extract is concentrated and added to alcoholic ammonia or alcoholic potassium hydroxide, when the salt crystallises out. From 100 grams of the product prepared under the best conditions, about 15 grams of the crude ammonium salt can be obtained.

*Analysis of the Product; Nitroform, Nitrous and Nitric Acids.*  
—The estimation of nitrous acid cannot be made directly on the product, for other substances which reduce permanganate are present. Two procedures have been followed. The permanganate titre of the product diluted 1 in 10 is determined; then either the nitrous acid is removed by aspiration or by boiling with ammonium nitrate (Gailhat, *J. Pharm. Chim.*, 1900, [vi], 12, 9; Gerlinger, *Zeitsch. angew. Chem.*, 1902, 14, 1250; they both use ammonium chloride). In the aspiration, it is not necessary to remove the whole of the nitrous acid, which is a very lengthy process. At a

given temperature and with a given air current, the percentage loss of nitrous acid from the solution follows the well-known law, and is independent of the initial concentration. At 16°, with the rate of air current 0.1 litre per minute, trials with known solutions of nitrous acid at various concentrations in aqueous nitric acid, and with known solutions of nitroform and nitrous acid in 7–8 per cent. nitric acid, show that 73.3 (72.8–73.9) per cent. of nitrous acid disappear in one hour. After the partial removal of the nitrous acid by aspiration or the complete removal by ammonium nitrate, the residual permanganate titre is determined, whence the “nitrous acid” can be calculated. Determinations of the nitrous acid made by these two methods agree fairly well, but the method of aspiration is probably the more trustworthy.

*Determination of Nitroform.*—Nitroform can be titrated in aqueous solution by alkali hydroxide in the presence of phenolphthalein (Hantzsch and Rinckenburger, *Ber.*, 1899, **32**, 631). We have devised a method, depending on the reduction of permanganate in the presence of sulphuric acid, which will be discussed more fully in another place. Recently, Erich Schmidt (*Ber.*, 1919, **52**, [B], 400) has described a procedure in which nitron is used as precipitant; this we have not yet tested, nor would it be easily applicable to our conditions, owing to the presence of nitric acid.

The product contains, besides nitrous acid and nitroform, other substances (for example, oxalic acid) which reduce permanganate. After removal of the nitrous acid, the nitroform may be extracted with ether and then titrated, or, preferably, distilled off and titrated with permanganate.

The following is a typical analysis: 2–5 c.c. of the “product” are added to 18–45 c.c. of  $N/2$ -V-alkali hydroxide; 5 c.c. are diluted with 10–15 c.c. of water, and 2–3 grams of ammonium nitrate added. The mixture is gently boiled for several minutes (five to ten), and then diluted to 100 c.c., acidified with 5–10 c.c. of 10 per cent. sulphuric acid, and distilled until the distillate is colourless (thirty minutes). The distillate may be collected in water or  $N/10$ -alkali; it is finally titrated with  $N/10$ - $\text{KMnO}_4$ . One c.c. of  $N/10$ - $\text{KMnO}_4$  is equivalent to  $151/80,000 = 0.0019$  gram of nitroform.

After destruction of nitrous acid and extraction of nitroform by ether, the residue still reduces permanganate. The reduction is but small under conditions most favourable for the preparation of nitroform or tetranitromethane. Some, and sometimes most, of the reduction of the permanganate by the residue is to be attributed to oxalic acid.

A rough estimate of the nitric acid in the product can be made

by deducting from the total alkali titre the alkali titre equivalent to the permanganate titre of the diluted product. As this deduction does not amount to more than 10 per cent. of the total alkali titre, a rough estimate of the nitric acid remaining is possible.

In a typical experiment, in which 4.27 litres of acetylene were absorbed by 138.6 grams of nitric acid (diluted to 95 per cent.), about 75 grams of nitric acid remained in the product, which weighed 123.5 grams. Deducting nitric acid, nitrous acid, and nitroform, the water in the product comes to 30 grams.

*Analysis of Gases evolved during the Interaction of Acetylene and Nitric Acid.*—The gas coming from the bubbler (B) is collected over a neutral, saturated calcium chloride solution in a large vessel of known capacity; the last part of the gas in an experiment is measured in a graduated vessel. Both carbon dioxide and acetylene are less readily soluble in saturated calcium chloride than in other saline solutions; at 14°, carbon dioxide has a solubility of 0.1 in 1, and acetylene 0.08 in 1, by volume.

The gas evolved during the heating of the product with sulphuric acid was collected in a similar manner. The liquid nearly filled the flask, which was ground on to a narrow condenser tube; this tube was carried on as a delivery tube for the evolved gas.

Table IV shows the large volumes of gas (carbon dioxide) collected. Nine-tenths, or rather more, are evolved during the interaction of acetylene and nitric acid when mercury is present, and the remainder during the heating with sulphuric acid. In the absence of mercury,  $2/3$ – $3/4$  of the gas passes off at the first stage, and  $1/4$ – $1/3$  at the second stage. These ratios strictly apply only to the carbon dioxide, which, however, largely predominates, especially in the first stage, less exactly to the total gas. The gas consists in the main of carbon dioxide with small percentages of acetylene and carbon monoxide, and traces of air. The gas given off in the heating contains much oxygen (up to 40–50 per cent.) from the interaction of nitric and sulphuric acids.

The gas was analysed in a "Bone and Wheeler" apparatus. The acetylene was absorbed by a 5 per cent. solution of potassium bromide saturated with bromine; the absorption is somewhat slow towards the end, but complete. After removal of the bromine vapour by the alkaline reagent, the carbon monoxide is absorbed by the ammoniacal cuprous chloride reagent. We have tested exhaustively this procedure on known mixtures of gases, and found it quite accurate. Usually, the gas of the first stage will contain:  $\text{CO}_2 = 75$ –80,  $\text{C}_2\text{H}_2 = 5$ –6,  $\text{CO} =$  at most 1 per cent.

*Preparation of Tetranitromethane.*—Originally, tetranitro

methane was prepared by Schischkov (*loc. cit.*) from trinitroacetone. Later, it was obtained in the exhaustive nitration of aromatic hydrocarbons (Will, *Ber.*, 1914, **47**, 704; Claessen, D.R.-P. 184229) by the action of diacetylorthonitric acid or acetyl nitrate on acetic anhydride (Pictet and Genequand, *loc. cit.*; Pictet and Khotinsky, *Compt. rend.*, 1907, **144**, 210), or from nitrogen pentoxide on acetic anhydride (Schenck, D.R.-P. 211198, 211199), or from nitric acid on acetic anhydride (Farbenfabriken vorm. F. Bayer & Co., D.R.-P. 224057; Berger, *Compt. rend.*, 1910, **151**, 813; Chattaway, T., 1910, **97**, 2099).

In preparing tetranitromethane from a hydrocarbon by exhaustive nitration, it is obvious that a low proportion of hydrogen to carbon, such as obtains in benzene, naphthalene, or acetylene, is desirable in order to economise nitric acid. Not only does the oxidation of a large proportion of hydrogen entail a corresponding loss of nitric acid, but the nitrating agent becomes diluted with water, and hence less efficient. On these grounds, benzene or its derivatives, or naphthalene derivatives, or acetylene are the most suitable substances. For various reasons, acetylene would be an excellent source of tetranitromethane. Whilst only some 4–5 per cent. of benzene nitrated can be converted into tetranitromethane, it has been shown in the foregoing that some 37 per cent. of the acetylene appears as this substance under suitable conditions.

The product from the interaction of acetylene and nitric acid contains very little tetranitromethane. If it is heated or first mixed with phosphoric oxide, sulphuric acid, or fuming sulphuric acid and then heated, tetranitromethane is formed.

A satisfactory procedure, in which all the nitroform is converted into tetranitromethane and the maximum yield is obtained, is to mix the product from 90 c.c. of 100 per cent. nitric acid with 190–380 grams of sulphuric acid or sulphuric acid containing 25 per cent. of sulphur trioxide. The sulphuric acid is added to the product, and care is taken that the temperature does not rise. The sulphuric acid from the bubbler (*B*), which contains a little nitroform, is also introduced. The mixture may be then directly distilled, but it is preferable to heat it, finally to 90–95°, under reflux until gas ceases to be evolved; this operation usually occupies about four hours. For reasons given in the foregoing, it is important that the product is mixed with sulphuric acid as soon as possible after the passage of the acetylene. That this mixture should then be kept for some time before heating or distilling is immaterial.

On cooling, much of the tetranitromethane will appear as an



oil, or even crystals; it may be collected by means of carbon tetrachloride or petroleum, but isolation by distillation is simplest.

The effect of certain variations in this procedure may be noted. The proportion of sulphuric acid may even be reduced below the limits given in the foregoing without producing any considerable diminution in the yield. Even if the proportion  $\text{H}_2\text{SO}_4:\text{HNO}_3 \approx 0.75:1$  by weight, the yield of tetranitromethane is only reduced by 10 per cent. The heating or the distillation of such a mixture is, however, attended with risk, as sudden decomposition, with evolution of gas, may ensue.

The addition of 20–25 grams of nitric acid to the mixture of the product and sulphuric acid before heating or distilling leads to an improvement of the yield (some 10 per cent.), especially if the conditions have otherwise been unfavourable; for example, if an excessive volume of acetylene has been passed into the nitric acid, or the temperature has been low, or the nitric acid too dilute. Under the conditions outlined in the foregoing, such addition of nitric acid has little, if any, effect.

As examples of the operation, the two following may be cited. The largest quantity of tetranitromethane (23.2 grams: 410 per cent. on the acetylene) in one operation was obtained by passing 5 litres into 138.6 grams (90 c.c.) of absolute nitric acid at  $30^\circ$  with 0.55 gram of mercuric nitrate in suspension. A better yield, of 453 per cent., was obtained by passing 4.6 litres into the same quantity of nitric acid diluted with water to 95 per cent. at the same temperature and with the same quantity of mercuric nitrate in solution; the weight of tetranitromethane isolated was 22.3 grams.

*The Purification and Properties of Tetranitromethane.*—The crude material, after washing with water, is nearly colourless, and melts at  $13.4\text{--}13.5^\circ$ . Thorough washing with dilute aqueous sodium carbonate does not change the melting point. After partial freezing and pouring off the remaining liquid three times, the substance melted at  $13.75^\circ$ , and the melting point was not raised by further fractionation. It has  $D_{15}^{20} 1.65009$ .

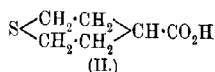
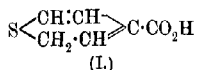
UNIVERSITY COLLEGE OF N. WALES,  
BANGOR.

[Received, January 14th, 1920.]

XXXVII.—*Synthetical Experiments with  $\beta\beta'$ -Dichloroethyl Sulphide.*

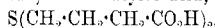
By WILLIAM DAVIES.

A CONSIDERATION of the formula of penthiophencarboxylic acid (I)



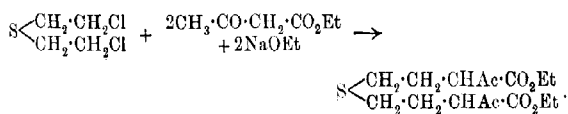
leads to the expectation that this acid would show properties analogous to those exhibited by benzoic acid. In order to test this hypothesis and with the object of synthesising penthiophencarboxylic acid, an attempt was made to condense  $\beta\beta'$ -dichloroethyl sulphide with ethyl sodiomalonate, when it was expected that ethyl 1-thiopentamethylene-4:4-dicarboxylate would be produced, and that this ester, on hydrolysis and elimination of carbon dioxide, would yield 1-thiopentamethylene-4-carboxylic acid (II). This, on successive bromination and elimination of hydrogen bromide, should furnish the desired penthiophencarboxylic acid.

The condensation with ethyl malonate proceeded, however, in a different direction, as was evident from the fact that the product of the reaction, namely, ethyl  $\gamma$ -thiodiethylmalonate (which could not be obtained in a pure state), on hydrolysis and elimination of carbon dioxide, yielded  $\gamma$ -thiodibutyric acid,



This acid was obtained in shining leaves melting at  $97-98^\circ$ , and for a dibasic acid is surprisingly sparingly soluble in cold water. It had already been described by Gabriel (*Ber.*, 1890, **23**, 2493), who prepared it (m. p.  $99^\circ$ ) by hydrolysing the nitrile obtained by heating  $\gamma$ -chlorobutyronitrile with potassium sulphide.

Since the malonic ester condensation did not give the desired result,  $\beta\beta'$ -dichloroethyl sulphide was condensed with ethyl sodioacetate, and the condensation product submitted to alkaline hydrolysis. The acid isolated was again  $\gamma$ -thiodibutyric acid, showing that the condensation had resulted in the formation of ethyl  $\alpha\alpha'$ -diaceto- $\gamma$ -thiodibutyrate, thus:



On alkaline hydrolysis this ester is decomposed in the usual manner to produce  $\gamma$ -thiodibutyric acid.

It is noteworthy that a much better yield of  $\gamma$ -thiodibutyric acid was obtained in the condensation with ethyl acetoacetate than in the corresponding experiment with ethyl malonate.

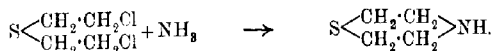
The conditions of experiment in the condensation with these two esters were varied (see pp. 302, 304), but in no case was there any evidence of ring-formation. The attempt to synthesise 1-thiopentamethylene-4-carboxylic acid had therefore to be abandoned.

Experiments were next made on the action of potassium cyanide on  $\beta\beta'$ -dichloroethyl sulphide in the hope of obtaining  $\beta\beta'$ -dicyanoethyl sulphide,  $S(CH_2 \cdot CH_2 \cdot CN)_2$ .

The nitrile obtained, however, was found to possess the abnormal formula  $C_6H_{12}S_2(CN)_2$ , and yielded on hydrolysis the acid,  $C_6H_{12}S_2(CO_2H)_2$ . It is possible that the nitrile has the composition  $CN \cdot CH_2 \cdot CH_2 \cdot S \cdot CH_2 \cdot CH_2 \cdot S \cdot CH_2 \cdot CH_2 \cdot CN$ , but the matter has not been further investigated.

The next experiments were made with the object of preparing tetrahydrothiophen by the action of metals, especially sodium, on  $\beta\beta'$ -dichloroethyl sulphide. Molecular sodium has, however, no action on the dichloro-derivative in boiling xylene, and when sodium is heated with it without diluent, there is no sign of reaction until the mixture is boiled, and then the sodium suddenly takes fire and forms sodium sulphide as well as sodium chloride. Boiling the dichloro-derivative with molecular silver and with finely divided copper also gave a negative result.

The action of  $\beta\beta'$ -dichloroethyl sulphide on ammonia was then investigated, with the object of preparing 1:4-thiazan, thus:



Several alkylthiazans have already been prepared from  $\beta\beta'$ -dichloroethyl sulphide by the action of amines (Clarke, T., 1912, 101, 1583), but the parent substance has not been described.

$\beta\beta'$ -Dichloroethyl sulphide reacts only sluggishly with dry gaseous ammonia, even at  $150^\circ$ . On the other hand, when heated with excess of alcoholic ammonia under pressure at  $60^\circ$ , it is readily converted into 1:4-thiazan. Thiazan is a colourless liquid with a characteristic odour and boils at  $169^\circ/758$  mm., or  $5^\circ$  higher than methylthiazan as recorded by Clark (*loc. cit.*). It has most of the properties common to organic bases, but the *platinichloride* has the formula  $B, HCl, PtCl_4$ , and the mode of formation of the *hydrochloride* (see p. 307) tends to show that the sulphur atom, as well as the imino-group, can attach hydrogen chloride. Thiazan reacts

readily with potassium, and the *picrate* and *picrolonate* are characteristic, crystalline substances melting at  $198^{\circ}$  and  $242^{\circ}$  respectively. Thiazan combines with one molecule only of ethyl iodide, yielding a crystalline *ethiodide*.

The sulphone and sulphoxide corresponding with  $\beta\beta'$ -dichloroethyl sulphide (compare Spica, *Gazzetta*, 1919, **49**, ii, 299) are colourless, crystalline substances which do not possess the characteristic physiological properties of the parent sulphide, but the sulphone, especially in the form of fine dust, causes sneezing.

The  $\beta\beta'$ -dichloroethyl sulphide used in these experiments was kindly supplied by the Manager of the Avonmouth factory, where it was made by the sulphur monochloride process. It is noteworthy that it contained about 0.5 per cent. of diethylene disulphide, whilst the German "mustard gas," made by the thiodiglycol process, contained very much more.

#### EXPERIMENTAL.

##### *Purification of $\beta\beta'$ -Dichloroethyl Sulphide.*

The crude substance is best purified by distillation in a vacuum, but the fraction of constant boiling point still contains a trace of diethylene disulphide. This can be practically completely removed by distillation under ordinary pressure, as the disulphide very readily sublimes at  $190^{\circ}$ , before the boiling point,  $217^{\circ}$ , of the dichloro-derivative has been reached. It is, however, more convenient to retain the small amount of impurity, and, after a reaction, to distil off the disulphide and unchanged dichloro-derivative in a current of steam.

The disulphide is very volatile, has a disagreeable odour, and melts at  $111^{\circ}$  (Found: C=39.8; H=6.8.  $C_4H_8S_2$  requires C=40.0; H=6.7 per cent.). It was conclusively identified by a determination of the melting point when mixed with the diethylene disulphide (m. p.  $111^{\circ}$ ), obtained by boiling alcoholic sodium sulphide with ethylene dichloride (compare Masson, T., 1886, **49**, 235).

Pure  $\beta\beta'$ -dichloroethyl sulphide boils at  $120^{\circ}/34$  mm. and  $122.5^{\circ}/37$  mm., and readily solidifies in cold weather, forming long, colourless needles, which melt at  $13.5^{\circ}$  to a liquid having a density of about 1.28 at the ordinary temperature. It is very sparingly soluble in water (compare Hopkins, *J. Pharm. Expt. Ther.*, 1919, **12**, 393), but can be readily hydrolysed by boiling alcoholic sodium hydroxide solution. This reagent and nitric acid are convenient substances with which to clean vessels that have contained  $\beta\beta'$ -dichloroethyl sulphide.

The sulphone is formed in almost theoretical amount by adding  $\beta\beta'$ -dichloroethyl sulphide to excess of fuming nitric acid (D 1.50), the vigorous reaction being completed by cautiously boiling for a short time. On cooling, pouring into water, and keeping overnight, the sulphone is precipitated, and crystallises from alcohol in colourless, lustrous laminae melting at  $53.5^\circ$ . An incautious smell of the crystals may cause violent sneezing. The sulphone is volatile in steam. As it is extremely difficult to detect the chlorine by the ordinary sodium test, it is better to reduce the sulphone by sodium in alcohol prior to testing (Found: C=25.3; H=4.2; S=16.9.  $C_4H_8O_2Cl_2S$  requires C=25.1; H=4.2; S=16.75 per cent.).

The sulfoxide is formed quantitatively by gradually adding  $\beta\beta'$ -dichloroethyl sulphide to excess of cold ordinary nitric acid and allowing the solution to remain for twenty-four hours at the ordinary temperature. The liquid is then rendered slightly alkaline by sodium carbonate, and the sulfoxide is precipitated. It separates from alcohol in colourless crystals melting at  $109.5^\circ$ . It dissolves readily in organic solvents, but is only sparingly soluble in water, which it renders faintly alkaline (Found: C=27.3; H=4.5.  $C_4H_8OCl_2S$  requires C=27.4; H=4.6 per cent.).

*Condensation of Ethyl Sodiomalonate with  $\beta\beta'$ -Dichloroethyl Sulphide.*

To a mixture of  $\beta\beta'$ -dichloroethyl sulphide (25 c.c.: 1 mol.) and ethyl malonate (68 c.c.: 5 per cent. excess of 2 mols.) was slowly added a cold solution of sodium ethoxide prepared from 9.8 grams of sodium (5 per cent. excess of two atoms) in 150 c.c. of absolute alcohol. There was a slight evolution of heat, the liquid became cloudy, and with occasional shaking during half an hour the contents of the flask became almost solid through the deposition of sodium chloride. The product was allowed to remain overnight, the reaction completed by boiling for one hour on the water-bath, the alcohol distilled off, and the residual white mass treated with 150 c.c. of water and distilled in a current of steam. A little unchanged ethyl malonate passed over, together with a trace of diethylene disulphide.

There remained in the flask a heavy oil, which was extracted with ether. The ethereal solution was dried and evaporated, when the residual oil weighed 45 grams. This oil, which undoubtedly consisted largely of ethyl  $\gamma$ -thiodiethylmalonate, was a very pale yellow liquid with a not unpleasant odour somewhat reminiscent

of celery. As it decomposed on attempted distillation under diminished pressure, it could not be obtained in a pure state. Since its hydrolysis by aqueous or alcoholic alkali is liable to be very violent, aqueous alkali was at first employed, and the following procedure adopted.

The ester (15 grams) was poured into 100 c.c. of sodium hydroxide solution (47 per cent.), and the mixture shaken. The heat given out was sufficient to cause the liquid to boil gently, and this ebullition was maintained by the careful addition, with constant shaking, of a further 30 grams of the ester. The reaction having subsided, methyl alcohol (100 c.c.) was added, and the mixture boiled for two hours. After removing the ethyl and methyl alcohols by distillation, and cooling the gelatinous sodium salt which was formed, hydrochloric acid (200 c.c. of 30 per cent.) was added, and the thio-acid extracted six times with ether. The ethereal solution was dried and evaporated, leaving 17 grams of a brown syrup, which showed no tendency to solidify after scratching and keeping in a vacuum over sulphuric acid at  $0^{\circ}$  for a week. This crude acid was moderately soluble in water, and from it crystalline  $\gamma$ -thiodibutyric acid was obtained, in the following way. Carbon dioxide was eliminated by heating in an oil-bath for eight hours at  $150$ — $170^{\circ}$ , when effervescence had completely ceased. The dark residual acid solidified on cooling, and a sample crystallised from ether melted at  $40$ — $60^{\circ}$ . After boiling the ammonium salt of the acid with animal charcoal and repeatedly crystallising from water, the acid was obtained in colourless leaves with a nacreous lustre melting at  $97$ — $98^{\circ}$  (Found:  $C=46.0$ ;  $H=6.8$ .  $\text{Equiv.}=102.7$ .  $C_8H_{14}O_4S$  requires  $C=46.6$ ;  $H=6.8$  per cent.  $\text{Equiv.}=103$ ).

$\gamma$ -Thiodibutyric acid is fairly readily soluble in hot water, very sparingly so in cold, but in order to obtain the acid in a crystalline condition, the aqueous solution employed must be dilute, otherwise, on cooling, the acid is precipitated as a brown oil. The acid is moderately soluble in alcohol, ether, or benzene, and crystallises from the last-named in microscopic plates on adding light petroleum. The acid does not distil in a current of steam or under diminished pressure. The ammonium salt slowly decomposes, with precipitation of the acid, when its aqueous solution is allowed to remain for several weeks.

*Ethyl  $\gamma$ -Thiodibutyrate.*

In order to ascertain whether the crude thiodibutyric acid contained any cyclic monobasic acid, the acid left after elimination of

carbon dioxide was esterified, and the ester fractionally distilled. The crude acid (41 grams), prepared from 100 c.c. of dichloroethyl sulphide and 272 c.c. of ethyl malonate, was esterified by boiling for three and a-half hours with 200 c.c. of absolute alcohol and 30 c.c. of concentrated sulphuric acid. The product was poured into water, extracted with ether, and the ethereal solution washed with sodium hydroxide solution and dried over calcium chloride.\* On distilling the ester, the first fraction, apart from a trace of diethylene disulphide boiling at  $107^{\circ}/23$  mm., consisted of 20 grams, which passed over at  $180\text{--}200^{\circ}/23$  mm. On redistillation, 17 grams of this fraction were obtained at  $188\text{--}197^{\circ}/23$  mm., mostly at  $196^{\circ}$ . The viscous, residual ester in the flask could not be distilled without decomposition, and has not been investigated.

*Ethyl  $\gamma$ -thiodibutyrate* is a colourless liquid with a disagreeable odour, insoluble in water, and readily miscible with organic solvents. It boils at  $185^{\circ}/11$  mm. and  $196^{\circ}/23$  mm., and has  $n_D^{20}$  1.4701. On hydrolysis,  $\gamma$ -thiodibutyric acid (m. p.  $97\text{--}98^{\circ}$ ) is formed:

0.0953 gave 0.1941  $\text{CO}_2$  and 0.0738  $\text{H}_2\text{O}$ . C=55.6; H=8.6.

0.1387 „ 0.1224  $\text{BaSO}_4$ . S=12.1.

$\text{C}_{12}\text{H}_{22}\text{O}_4\text{S}$  requires C=55.0; H=8.4; S=12.2 per cent.

*Condensation of  $\beta\beta'$ -Dichloroethyl Sulphide with Ethyl Sodiummalonate in the Absence of Alcohol.*

In order to avoid any hydrolytic action of sodium ethoxide on the dichloro-derivative which may have taken place, even in the cold, the condensation was carried out in the following way. Ethyl malonate (136 c.c.) dried over calcium chloride was added to molecular sodium (20 grams) in boiling xylene. Dry benzene was added, and the mixture boiled gently on the water-bath. After four hours, all the sodium had disappeared, giving rise to the gelatinous ethyl sodiummalonate.  $\beta\beta'$ -Dichloroethyl sulphide (50 c.c.) was slowly added with shaking, and the benzene solution boiled for ten hours. The benzene was then removed, water added, the mixture distilled in a current of steam, and the residual ester worked up as before. The yield of ethyl  $\gamma$ -thiodibutyrate was better

\* In the first esterification the catalyst used was hydrogen chloride, and the resulting ester showed the physiological properties of "mustard gas," although there was not sufficient present to be separated by fractional distillation. This trace of  $\beta\beta'$ -dichloroethyl sulphide was clearly formed by the action of hydrogen chloride on some thiodiglycol, doubtless obtained by the hydrolytic action of the slightly alkaline ethyl sodiummalonate on the dichloro-derivative. Since the unexpected formation of  $\beta\beta'$ -dichloroethyl sulphide even in trifling amount is dangerous, sulphuric acid has been used as the catalyst in all esterifications.

than in the former experiment, the fraction b. p. 180—200°/23 mm. weighing 12 grams. No other fraction was obtained.

*Condensation of  $\beta\beta'$ -Dichloroethyl Sulphide with Ethyl Sodioacetacetate.*

A cold solution of sodium ethoxide, prepared from 20 grams of sodium and 300 c.c. of absolute alcohol, was added to a mixture of 50 c.c. of  $\beta\beta'$ -dichloroethyl sulphide and 120 c.c. of ethyl acetacetate. There was a slight evolution of heat, and the reaction was facilitated by shaking. The contents of the flask set to a white mass in half an hour, and, after remaining overnight, the reaction was completed on the water-bath, the alcohol removed, water added, and the mixture distilled in a current of steam. The heavy oil, non-volatile in steam, was extracted with ether, dried, and found to weigh 127 grams (120 c.c.). It decomposed on attempted distillation under diminished pressure.

*Hydrolysis of the Ethyl Acetacetate Derivative with Alkali.*

The 127 grams of the above ester were slowly added to 430 c.c. of 20 per cent. methyl-alcoholic sodium hydroxide. Frothing took place, but the hydrolysis was not nearly so vigorous as in the case of the condensation product from ethyl malonate. The hydrolysis was completed by boiling for six hours on the water-bath, and the acetone methyl and ethyl alcohols were distilled off, the mass of sodium salt being extracted with ether (extract A) to remove any thioketone, and then acidified by the addition of 350 c.c. of concentrated hydrochloric acid. An oil was precipitated, which was extracted three times with ether, the ethereal solution being dried and evaporated. The brown acid weighed 47 grams, and began to crystallise after remaining at 0° in a vacuum over phosphoric oxide. The acid was esterified by boiling for three hours with 150 c.c. of alcohol and 15 c.c. of sulphuric acid, and yielded 40 grams of ester, which gave 19 grams of a fraction boiling at 184—192°/11 mm., mostly at 185°, and having  $n_D^{20}$  1.4699. The residual, viscous ester in the flask began to decompose on attempted distillation (Found: S=12.6.  $C_{12}H_{22}O_4S$  requires S=12.2 per cent.). On hydrolysis, the ester furnished  $\gamma$ -thiodibutyric acid, identical with that obtained from ethyl malonate, as shown by a mixed melting-point determination.

The methyl ester was prepared from the crude acid in order to obtain an ester with lower boiling point, and thus, so far as possible, to avoid decomposition on distillation. There was still,

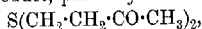


however, a large amount of residual ester, which could not be distilled, and the yield of methyl ester was the same as that of the ethyl ester. *Methyl  $\gamma$ -thiodibutyrate* boils at  $170^{\circ}/20$  mm., has  $n_D^{20}$  1.4791, and is similar in properties to the ethyl ester:

0.2465 gave 0.2497  $\text{BaSO}_4$ .  $S=13.9$ .

$\text{C}_{10}\text{H}_{18}\text{O}_4\text{S}$  requires  $S=13.7$  per cent.

The ethereal extract (A) contained a small quantity of an oil with an odour not unlike peppermint. There was, however, insufficient of this by-product, probably the thiodiketone,



for its examination.

Two modifications of the ethyl acetoacetate condensation were tried. In the first case, no alcohol was used, the ethyl sodioacetoacetate being in suspension and solution in benzene. In the second case, the sodium ethoxide was added to the dichloroderivative mixed with one-half the quantity of ethyl acetoacetate used in the preceding experiments. After remaining for three hours in the cold, when some salt was deposited, the remaining half of the ethyl acetoacetate was added, and the product worked up after remaining overnight. Ethyl  $\gamma$ -thiodibutyrate alone was isolated. This confirms the common observation that the tendency to form the ring or open chain is not dependent on the relative amounts of the dihaloid and ethyl sodioacetoacetate.

In these last two experiments, the condensation product was not distilled in a current of steam, and, with this exception, was worked up as before. The only ester obtained, however, was ethyl  $\gamma$ -thiodibutyrate.

#### *The Action of $\beta\beta'$ -Dichloroethyl Sulphide on Potassium Cyanide.*

In studying this reaction, care was taken to carry it out under conditions as anhydrous as possible, absolute alcohol being used in order to reduce the hydrolytic action of the potassium cyanide to a minimum. Thirty-five grams of finely powdered potassium cyanide (about 30 per cent. excess) were mixed with 250 c.c. of absolute alcohol, and 25 c.c. of  $\beta\beta'$ -dichloroethyl sulphide added. No signs of a reaction were observed on shaking, but when the liquid was boiled, it soon turned brown, and white crusts, presumably of potassium chloride, adhered to the sides of the flask. The boiling was continued with occasional shaking for seven hours, and, while still hot, the alcoholic solution was filtered from insoluble inorganic matter. The precipitate was extracted with boiling alcohol and filtered, the filtrates mixed, and most of the alcohol distilled off. On cooling, the residual liquid set to a brown,

oily mass, which was collected and crystallised from methyl alcohol. Small, brown crystals formed which, on recrystallisation from acetone and then from benzene, melted at  $87-88^\circ$ , although the crystals were still slightly brown. The substance was obtained in colourless, microscopic crystals, melting at  $91-91.5^\circ$ , by dissolving in benzene, precipitating, and repeating this procedure several times.

The yield of this substance was poor, 25 c.c. (about 32 grams) of  $\beta\beta'$ -dichloroethyl sulphide furnishing 7 grams of the crude crystals melting at  $87-88^\circ$ . It is very readily soluble in methyl and ethyl alcohols, acetone, or benzene, moderately so in chloroform, and sparingly so in cold ether or light petroleum. It is insoluble in water, non-volatile in steam, and is rapidly hydrolysed by dilute boiling sodium hydroxide solution, ammonia being evolved in the process. It is insufficiently soluble in cold benzene or acetic acid for the molecular weight to be determined in these solvents by the cryoscopic method, and thus it became necessary to resort to naphthalene as a solvent, and also to the much less accurate ebullioscopic method:

0.1216 gave 0.2130  $\text{CO}_2$  and 0.0647  $\text{H}_2\text{O}$ .  $\text{C}=47.8$ ;  $\text{H}=5.9$ .

0.1152 „ 13.9 c.c.  $\text{N}_2$  at  $15^\circ$  and 757 mm.  $\text{N}=14.1$ .

0.3800 required 38.5 c.c.  $\text{N}/10\text{-NaOH}$  for hydrolysis.  
 $\text{N}(\text{as } \text{NH}_3)=14.2$ .

0.2393 gave 0.5645  $\text{BaSO}_4$ .  $\text{S}=32.4$ .

0.376 in 17.83 naphthalene gave  $\Delta t = -0.70^\circ$ .  $\text{M.W.}=206$ .

The elevation of the boiling point of ethyl alcohol gave values for the molecular weight varying between 180 and 220.

$\text{C}_5\text{H}_9\text{N}_2\text{S}_2$  requires  $\text{C}=48.0$ ;  $\text{H}=6.0$ ;  $\text{N}=14.0$ ;  $\text{S}=32.0$  per cent.  $\text{M.W.}=200$ .

On hydrolysis with dilute alkali, this nitrile was quantitatively converted into the corresponding acid, which was surprisingly sparingly soluble in cold organic solvents, except methyl and ethyl alcohols. It was moderately soluble in boiling xylene, and very rapidly precipitated on cooling. When dissolved in hot water and the solution cooled, the acid very slowly crystallised in pearly leaves which melted at  $151-153^\circ$ . This acid, like  $\gamma$ -thiodibutyric acid, was sparingly soluble in cold water:

0.1390 gave 0.2047  $\text{CO}_2$  and 0.0733  $\text{H}_2\text{O}$ .  $\text{C}=40.2$ ;  $\text{H}=5.9$ .

0.3733 „ 0.7175  $\text{BaSO}_4$ .  $\text{S}=26.4$ .

0.1650 neutralised 13.9 c.c.  $\text{N}/10\text{-NaOH}$ .  $\text{Equiv.}=119$ .

$\text{C}_8\text{H}_{14}\text{O}_4\text{S}_2$  requires  $\text{C}=40.3$ ;  $\text{H}=5.9$ ;  $\text{S}=26.9$  per cent.

$\text{Equiv.}=119$ .

As already mentioned, it is possible that the acid has the con-

stitution  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and it is hoped shortly to prepare an acid having the above formula.

Since  $\beta\beta'$ -dicyanoethyl sulphide had not been isolated, the attempt to prepare a six-membered ring containing five carbon atoms and one sulphur atom was relinquished.

#### 1:4-Thiazan.

A mixture of 32 c.c. of  $\beta\beta'$ -dichloroethyl sulphide and 150 c.c. of freshly prepared 9 per cent. alcoholic ammonia was heated at  $60^\circ$  under pressure for four hours. By that time a mass of colourless crystals had separated, and the reaction was completed by heating at  $100^\circ$  for a further four hours. The crystals were washed out with a little water, in which they were very readily soluble, excess of ammonia was expelled by warming on the water-bath, and the brown solution acidified by hydrochloric acid. This liquid was then distilled in a current of steam in order to drive off alcohol and any unchanged  $\beta\beta'$ -dichloroethyl sulphide. After cooling, the contents of the flask were rendered strongly alkaline by means of sodium hydroxide, and a small quantity of oil separated. The alkaline solution was extracted fourteen times with ether, the ethereal solution dried and evaporated, and the residual red oil (15 grams) distilled. About 9 grams of a fraction boiling at  $166\text{--}180^\circ/758$  mm. were collected, a large quantity of dark-coloured liquid being left in the distilling flask. On redistillation, 5 grams of a colourless liquid boiling at  $168\text{--}170^\circ/758$  mm. were obtained. This was finally distilled over solid sodium hydroxide and boiled at  $169^\circ/758$  mm.

1:4-Thiazan is a colourless liquid, miscible with water and organic solvents, and has an odour similar to, and yet more unpleasant than, that of pyridine. It is a very strong base, fumes in acid vapours, and very rapidly absorbs carbon dioxide from the air. When a drop was placed on a watch-glass, a scum was formed on its surface in a few seconds, and in the course of twenty minutes a non-deliquescent, white mass was produced, which dissolved with effervescence in dilute hydrochloric acid. Thiazan reacts vigorously with potassium on gentle warming, and hydrogen and a yellowish-brown solid are produced.

Thiazan boils at  $169^\circ/758$  mm. and  $166\text{--}167^\circ/743$  mm. It is noteworthy that this is slightly higher than the boiling point of the methyl derivative, namely,  $163\text{--}164^\circ/757$  mm. (Clarke, *loc. cit.*, p. 1586):

0.1261 gave 0.2195  $\text{CO}_2$  and 0.0961  $\text{H}_2\text{O}$ .  $\text{C}=47.5$ ;  $\text{H}=8.45$ .

0.1641 „ 18.7 c.c.  $\text{N}_2$  at  $11^\circ$  and 760 mm.  $\text{N}=13.6$ .

0.1378 „ 0.3077  $\text{BaSO}_4$ .  $\text{S}=30.7$ .

$\text{C}_4\text{H}_9\text{NS}$  requires  $\text{C}=46.6$ ;  $\text{H}=8.7$ ;  $\text{N}=13.6$ ;  $\text{S}=31.1$  per cent.

The *hydrochloride*,  $\text{C}_4\text{H}_9\text{NS.HCl}$ , was obtained in white clusters of needles by adding a solution of hydrogen chloride in benzene to a benzene solution of thiazan until the mixture was only faintly basic. This procedure was adopted because passing hydrogen chloride into a benzene solution of thiazan resulted in the needles at first formed being changed by the excess of acid to a yellow oil, insoluble in the benzene. This oil, on heating, gave off hydrogen chloride, and then, on cooling, the crystalline hydrochloride was regenerated. Probably the sulphur atom had developed latent basic properties and had taken up hydrogen chloride.

Thiazan hydrochloride, after being washed with benzene and dried in a vacuum over phosphoric oxide, was obtained in colourless, deliquescent crystals, which softened at  $145^\circ$  and melted at  $160-165^\circ$ :

0.2174 required 15.5 c.c.  $\text{N}/10\text{-AgNO}_3$ .  $\text{Cl}=25.3$ .

0.2192 gave 17.5 c.c.  $\text{N}_2$  at  $11^\circ$  and 760 mm.  $\text{N}=9.5$ .

$\text{C}_4\text{H}_9\text{NS.HCl}$  requires  $\text{Cl}=25.45$ ;  $\text{N}=10.0$  per cent.

The *platinichloride* was prepared by adding platinic chloride solution to thiazan dissolved in dilute hydrochloric acid, and slowly separated as a yellow precipitate, amorphous even when seen under the microscope. The precipitate was collected after remaining overnight, well washed with water, alcohol, and ether, and dried in a vacuum over phosphoric oxide and then at  $70^\circ$  in an air-oven. When dried at  $100^\circ$ , the platinichloride darkens and loses weight, although it does not melt below  $250^\circ$ . Owing to its insolubility, it could not be obtained crystalline:

0.1206 gave 0.0502 Pt. Pt=41.6.

$\text{C}_4\text{H}_9\text{NS.HCl.PtCl}_4$  requires Pt=40.9 per cent.

The *picrate* is best produced by adding a dilute solution of picric acid in alcohol to an alcoholic solution of thiazan. In this way, blunt, pale orange needles are rapidly formed, which, after being washed with alcohol and dried in a vacuum, are pure. If the base is added to the alcoholic solution of picric acid, the picrate is apt to separate at once as an amorphous, yellow precipitate, which is difficult to purify. The picrate is sparingly soluble in alcohol, but fairly readily so in acetone, and melts and decomposes at  $198^\circ$ :

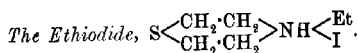
0.3045 gave 0.2189  $\text{BaSO}_4$ .  $\text{S}=9.9$ .

$\text{C}_4\text{H}_9\text{NS.C}_6\text{H}_3\text{O}_7\text{N}_3$  requires  $\text{S}=9.6$  per cent.

The *picrolonate* was prepared in a similar way to the picrate, and crystallised from alcohol in deep orange, short prisms. It darkened somewhat at 210°, and melted and decomposed to a very viscous liquid at 242°:

0.2095 gave 0.1376 BaSO<sub>4</sub>. S=9.0.

C<sub>4</sub>H<sub>9</sub>NS, C<sub>10</sub>H<sub>8</sub>O<sub>5</sub>N<sub>4</sub> requires S=8.7 per cent.



It was thought of interest to see whether the sulphur atom in 1:4-thiazan would develop its higher valency as easily as the nitrogen. It was noticed that when ethyl iodide was added to thiazan, a clear solution was formed, which rapidly became cloudy and, on keeping, deposited colourless crystals. The experiment was repeated by adding to thiazan a large excess of ethyl iodide mixed with an equal volume of alcohol, heating to boiling, and then allowing the mixture to remain in a desiccator overnight. A small quantity of colourless crystals separated, more being obtained on partial evaporation of the alcoholic solution. The substance was extremely soluble in water, moderately so in hot 90 per cent. alcohol, and sparingly so in cold absolute ethyl and methyl alcohols or in boiling pyridine. Other ordinary organic solvents had no appreciable solvent action. The dried crystals darkened at about 230°, but did not melt below 260°:

0.0608 gave 0.0553 AgI. I=49.1.

C<sub>6</sub>H<sub>14</sub>NIS requires I=49.4 per cent.

Only one molecule of ethyl iodide had therefore combined with one molecule of thiazan, the addition probably taking place at the nitrogen atom.

The author desires to express his gratitude to Prof. W. H. Perkin and Dr. E. Hope for the valuable advice he received from them in the course of this work. He also takes this opportunity of gratefully acknowledging a grant awarded him by the Board of Scientific and Industrial Research.

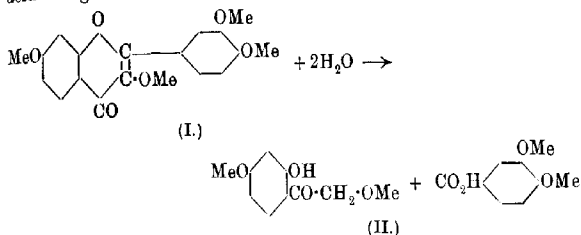
THE ORGANIC CHEMICAL LABORATORY,  
OXFORD.

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XXXVIII.—*Some Derivatives of Fisetol.*

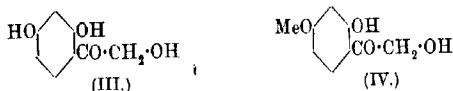
By WILLIAM KERSHAW SLATER and HENRY STEPHEN.

FISETOL DIMETHYL ETHER (II) was first isolated by Herzig (*Monatsh.*, 1891, **12**, 187) by boiling the tetramethyl ether of fisetin (I) with alcoholic potassium hydroxide, the dimethyl ether of protocathechuic acid being formed at the same time.



In a similar way, the tetraethyl ether of fisetin was found to give fisetol diethyl ether corresponding with II. At the present time, no fisetol derivatives of the type containing a free hydroxyl group in the  $\omega$ -position are known with certainty, and  $\omega$ -hydroxyresacetophenone (fisetol) (III), which possesses such a group, has not yet been described.

Tambor and Du Bois (*Ber.*, 1918, **51**, 748), however, claim to have isolated  $\omega$ -2-dihydroxy-4-methoxyacetophenone (fisetol 4-methyl ether) (IV) from  $\omega$ -bromoresacetophenone 4-methyl ether by conversion into the diacetate and subsequent hydrolysis of the latter.



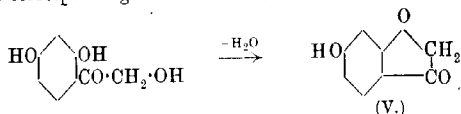
Sonn (*Ber.*, 1919, **52**, [B], 923) has cast some doubt on this result, and states that the product obtained by the action of acetic anhydride and sodium acetate on the corresponding  $\omega$ -chlororesacetophenone 4-methyl ether in the manner described by Tambor and Du Bois is the diacetate of 5-methoxycumaran-2-one. Auwers and Pohl (*Annalen*, 1914, **405**, 243) also obtained 5-methoxycumaran-2-one from the above chloro-compound by the action of hydrated sodium acetate in alcoholic solution.

It seems probable, also, that fisetol and derivatives of it containing a free hydroxyl group in the  $\omega$ -position will resemble the parent substance,  $\omega$ -hydroxyacetophenone (benzoylcarbinol), which is easily decomposed by warming in dilute acid or alkaline solutions.

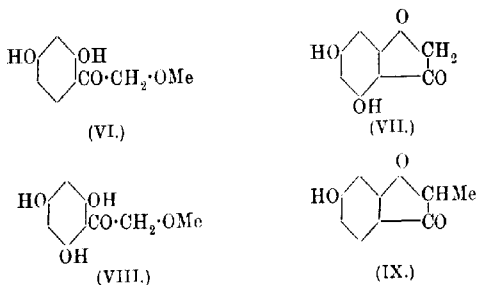
This is shown also by Herzig's attempt to obtain fisetol by demethylation of the dimethyl ether (II) by treatment with hydriodic acid, which only resulted in the formation of tarry matter.

Difficulties originating from the above statements have been experienced in the present work, the object of which was an investigation of the synthesis of fisetol derivatives by a general method of preparation.

The method depends on the synthesis of aromatic ketones devised by Hoesch (*Ber.*, 1915, **48**, 1122), which is an extension of Gattermann's synthesis of aromatic aldehydes. Hoesch has shown that the condensation of a nitrile with a phenolic compound leads to the formation of a ketimine of the type  $\text{CRR}'\text{:NH}\cdot\text{HCl}$ , which is easily hydrolysed to give the ketone,  $\text{R}\cdot\text{CO}\cdot\text{R}'$ . By condensing resorcinol with hydroxyacetonitrile, 5-hydroxycumaran-2-one (V) is formed, and not fisetol, as would be expected. This fact imposes a limitation on the method, and from our experiments it appears that the method is limited by the presence of hydroxyl groups in the ortho- and  $\omega$ -positions in the fisetol derivative formed in the reaction, a compound containing such groups being easily converted into the corresponding cumaran-2-one, as follows:



On the other hand, methoxyacetonitrile and resorcinol yield the stable fisetol derivative  $\omega$ -methoxyresacetophenone (VI). Phloroglucinol, on treatment with the same nitriles, gave 3:5-dihydroxycumaran-2-one (VII) and 2:4:6-trihydroxy- $\omega$ -methoxyresacetophenone (VIII) respectively.

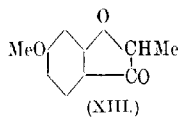
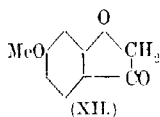
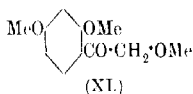
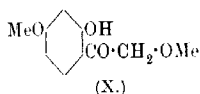


one (VIII) respectively. Acetaldehydecyanohydrin resembles hydroxyacetonitrile in its behaviour on condensation with resorcinol, yielding 5-hydroxy-1-methylcumaran-2-one (IX).

In carrying out the condensations, it was found that the presence of zinc chloride, as recommended by Hoesch, could be dispensed with, and it was only necessary to pass hydrogen chloride into a solution of methoxyacetonitrile and resorcinol in dry ether in order to bring about the formation of the crystalline ketimine hydrochloride, but the separation of the latter is only complete after the mixture has been allowed to remain for about five days in a refrigerator.

The condensations in which hydroxyacetonitrile and acetaldehydecyanohydrin were employed gave better results in the presence of zinc chloride, but the latter tends to cause decomposition during the isolation of the product unless considerable care is exercised. With reference to Hoesch's method, the preparation of resacetophenone has been repeated, using only resorcinol and acetonitrile in dry ether, and treating the resulting solution with dry hydrogen chloride. After remaining for five days in a refrigerator, the ketimine hydrochloride was decomposed in the usual way, and 94 per cent. of the theoretical yield of resacetophenone was obtained. Resorcinol dimethyl ether was found to give poor yields of 2:4-dimethoxyacetophenone, but these were much improved by the addition of zinc chloride to the mixture after treatment with hydrogen chloride, and then allowing to remain at the ordinary temperature for several days.

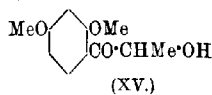
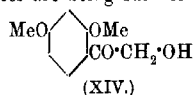
The following substances have been prepared in addition to those previously mentioned, and are described in a later part of the paper: 2-hydroxy-*o*-4-dimethoxyacetophenone (fisetol dimethyl ether) (X), *o*-2:4-trimethoxyacetophenone (fisetol trimethyl ether) (XI), 5-methoxycumaran-2-one (XII), and 5-methoxy-1-methylcumaran-2-one (XIII).



The condensations of resorcinol dimethyl ether with hydroxyacetonitrile and acetaldehydecyanohydrin, respectively, yielded products which were not isolated in a pure condition. The ketimine which was formed in each case, on treatment with water and warming, gave a white solid, which easily decomposed on concentrating the solution to obtain a further quantity of material. The amounts



obtained were in each case too small for further investigation, but the properties of each substance closely resembled those of the corresponding *o*-hydroxyacetophenone, and hence probably consisted of *o*-hydroxy-2:4-dimethoxyacetophenone (XIV) and 2:4-dimethoxyphenyl  $\alpha$ -hydroxyethyl ketone (XV). A brief description of the former only is given in the present paper, and both substances are being further investigated.



#### EXPERIMENTAL.

##### *Hydroxyacetonitrile*, $\text{HO}\cdot\text{CH}_2\cdot\text{CN}$ .

The method described by Polstorff and Meyer (*Ber.*, 1912, 45, 1911) for the preparation of hydroxyacetonitrile has been modified by substituting paraformaldehyde in place of commercial formaldehyde solution.

Potassium cyanide (32.5 grams:1 mol.) was dissolved in water (100 c.c.), and paraformaldehyde (15 grams) added in small portions, the temperature of the solution being maintained between  $0^\circ$  and  $5^\circ$ . The paraformaldehyde dissolved, and, after the requisite amount had been added, the clear solution was allowed to remain for one hour. The odour of formaldehyde had entirely disappeared by this time, the solution being then treated according to the method described by Polstorff and Meyer. Hydroxyacetonitrile was subsequently extracted from the aqueous solution by continuous extraction with ether in an apparatus designed for the purpose. The ethereal solution was dried with anhydrous sodium sulphate, two-thirds of the ether removed by distillation from a water-bath, and the remainder evaporated under diminished pressure. Slight decomposition takes place if the whole of the ether is removed on the water-bath. Pure hydroxyacetonitrile (29 grams) was obtained, which distilled at  $102^\circ/14$  mm.

##### *Methoxyacetonitrile*, $\text{MeO}\cdot\text{CH}_2\cdot\text{CN}$ .

Hydroxyacetonitrile, prepared as described above, was methylated by means of methyl sulphate according to the conditions given by Polstorff and Meyer (*loc. cit.*). The product boiled at  $120^\circ$ , and the yield from 15 grams of formaldehyde was 27 grams of the pure substance.

##### *o*-Methoxyresacetophenone (*Fisetol Methyl Ether*) (VI).

Resorcinol (6.5 grams:1 mol.) was dissolved in ether which had been previously dried (50 c.c.), and methoxyacetonitrile (5 grams:

1 mol.) added. A current of dry hydrogen chloride was passed through the solution for two hours, which was then allowed to remain overnight. A yellow, crystalline mass separated, consisting of the hydrochloride of the ketimine, and it was found in later experiments that the yield of this substance is increased by keeping the mixture for about five days in a refrigerator. The ether was poured off from the crystals, and the latter were washed twice with small quantities of dry ether and then dissolved in methyl alcohol, from which the ketimine hydrochloride separated as a fine, white, crystalline mass melting and decomposing at  $205-207^{\circ}$ :

0.1583 gave 9.2 c.c.  $N_2$  (moist) at  $17^{\circ}$  and 753 mm.  $N=6.67$ .

$C_9H_{11}O_3N.HCl$  requires  $N=6.45$  per cent.

The hydrochloride of the ketimine was dissolved in water and the solution warmed at  $80^{\circ}$  for half an hour, the colour changing to a claret-red; further heating caused a darkening of the solution with separation of tarry matter. At the end of the prescribed time, the solution was cooled, when a mass of crystals separated, and, after filtering and drying, the yield amounted to 8 grams, or about 70 per cent. of the theoretical. The substance crystallised from hot water in plates possessing a nacreous lustre, and melted at  $136^{\circ}$ . It is readily soluble in methyl or ethyl alcohols, ether, or benzene, and insoluble in light petroleum. With ferric chloride it gives a deep violet coloration, and reduces Fehling's solution, with the formation of a copper mirror. Tollens's reagent is also immediately reduced, with the precipitation of metallic silver:

0.1234 gave 0.2712  $CO_2$  and 0.0647  $H_2O$ .  $C=59.98$ ;  $H=5.82$ .

$C_9H_{10}O_4$  requires  $C=59.91$ ;  $H=5.5$  per cent.

The *p*-nitrophenylhydrazone was obtained by adding a solution of *p*-nitrophenylhydrazine in dilute acetic acid to an aqueous solution of  $\omega$ -methoxyresacetophenone. The hydrazone soon separated as a flocculent, yellow mass, which was immediately collected, and, after crystallisation from hot water containing a little ethyl alcohol, it melted and decomposed at  $205^{\circ}$ . On remaining in the air for several days, it becomes brick-red:

0.1596 gave 18.2 c.c.  $N_2$  (moist) at  $19^{\circ}$  and 769 mm.  $N=13.4$ .

$C_{15}H_{15}O_3N_3$  requires  $N=13.25$  per cent.

#### 2-Hydroxy- $\omega$ -4-dimethoxyacetophenone (X).

By methylating 1.8 grams of the compound described above with 1.2 grams (1 mol.) of methyl sulphate in 10 c.c. of 5 per cent. sodium hydroxide solution and keeping the solution cold in ice-water, acidifying with dilute hydrochloric acid, and concentrating, 1.5 grams of the monomethyl ether were obtained. After crystal-

ling from dilute alcohol, it was deposited in clusters of fine needles melting at 66°. There was no trace of the isomeric 4-hydroxy- $\omega$ -2-dimethoxyacetophenone.

A similar case has been observed by Hoesch (*loc. cit.*), who found that, on methylating resacetophenone with one molecular proportion of methyl sulphate, a quantitative yield of paeonol was obtained. 2-Hydroxy- $\omega$ -4-dimethoxyacetophenone was also obtained in the following manner.

Resorcinol monomethyl ether (3.2 grams:1 mol.) and methoxyacetonitrile (2.5 grams:1 mol.) were dissolved in dry ether (25 c.c.), and the solution was treated with a rapid stream of hydrogen chloride for one hour. Zinc chloride (1 gram) was now added, and the mixture allowed to remain for three days. A red oil separated, from which the ether was decanted, and the oil was washed twice with small quantities of ether. On treatment with water, it dissolved, and on warming the solution, small, colourless needles soon deposited. These were collected and dried, and found to be identical with the substance prepared by methylation, as above. After crystallisation from methyl alcohol, the substance melted at 66°, which in both cases agrees with that found by Herzig (*loc. cit.*).

#### $\omega$ -2:4-Trimethoxyacetophenone (XI).

This compound was prepared according to the method stated by Herzig, by methylating the substance just described with methyl iodide and potassium hydroxide solution, and crystallised from alcohol in fine, silky needles melting at 61—62°. Methylation of  $\omega$ -methoxyresacetophenone with two molecular proportions of methyl sulphate at 60° for eight hours produces the same substance, which separates from the alkaline solution. A higher temperature during the methylation causes much decomposition, with the formation of tarry material.

We have succeeded in preparing the above substance by condensing resorcinol dimethyl ether with methoxyacetonitrile. The process is similar to that already described. The yield, however, is poor: 5 grams of the dimethyl ether and 2.5 grams of the nitrile gave 1.4 grams of the product, that is, about 16 per cent. of the theoretical.

#### 5-Hydroxyeumaran-2-one (V).

This substance was prepared by treating 3 grams (1 mol.) of hydroxyacetonitrile and 5.5 grams (1 mol.) of resorcinol dissolved in 30 c.c. of dry ether to which a little zinc chloride was added. On passing a current of dry hydrogen chloride through the solution, a crystalline deposit separated after fifteen minutes, and after twenty-four hours the mixture was treated in the usual way.

The product, after crystallisation from hot water, in which it is sparingly soluble, was obtained in thin plates, which melted and decomposed at  $240^{\circ}$ , and gave no coloration with ferric chloride. (Found: C=63.74; H=4.06.  $C_8H_6O_2$  requires C=64.0; H=4.0 per cent.). The compound has already been described by Brühl and Friedländer (*Ber.*, 1897, **30**, 299). It reduces Fehling's solution in the cold, and with Tollens's reagent gives a silver mirror on warming.

On treatment with acetyl chloride (1 mol.), the acetyl compound was produced, which crystallised from dilute alcohol in leaves melting at  $81^{\circ}$ .

*5-Methoxycumaran-2-one (XII).*

All attempts to methylate 5-hydroxycumaran-2-one were unsuccessful, the action of methyl sulphate and of methyl iodide in alkaline solution producing a viscid, resinous mass. It was ultimately prepared by condensing resorcinol monomethyl ether with hydroxyacetoneitrile, and was the only product isolated from the reaction. No trace of  $\omega$ -4-dihydroxy-2-methoxyresacetophenone was found in the aqueous solution after the separation of 5-methoxycumaran-2-one, and rather less than a gram of the latter was obtained from 4 grams (1 mol.) of the ether and 2.5 grams (1 mol.) of nitrile. It crystallises from hot alcohol in pale straw-coloured needles melting at  $120^{\circ}$ , and has been fully described by Blom and Tambor (*Ber.*, 1905, **38**, 3589), Auwers and Pohl (*Annalen*, 1914, **405**, 264), and Sonn (*loc. cit.*).

*$\omega$ -Hydroxy-2:4-dimethoxyacetophenone (XIV).*

The condensation of hydroxyacetoneitrile with resorcinol dimethyl ether according to Hoesch's method gave a crystalline deposit when hydrogen chloride was passed into an ethereal solution of the two compounds. The deposit was dissolved in water, the solution concentrated by warming on the water-bath for a quarter of an hour, and finally by allowing to remain in a desiccator for two days. A fine, yellow, crystalline substance was deposited which, after being collected, was found to be only sparingly soluble in water, but readily so in alcohol. The dilute aqueous solution reduced Fehling's solution in the cold, giving cuprous oxide, and Tollens's reagent gave a precipitate of metallic silver. On boiling the substance with water, it appeared to be volatile in steam, a crystalline deposit being observed on the cool sides of the tube. On prolonged boiling (about five minutes), decomposition took place, with the formation of an oily scum. This decomposition occurred almost immediately in the presence of hydrochloric acid or sodium

hydroxide. The purest sample of the compound obtained melted and decomposed at 127–129°, but there was insufficient for an analysis.

*2:4:6-Trihydroxy- $\omega$ -methoxyacetophenone* (VIII).

This substance was readily obtained from the condensation of methoxyacetonitrile and anhydrous phloroglucinol in the usual way. The intermediate ketimine hydrochloride was isolated as a white, crystalline powder after crystallisation from methyl alcohol, which decomposed without melting between 238° and 241°. On boiling it with water, a clear solution was obtained, from which fine, silky needles separated on cooling. These were collected and recrystallised from hot water, and after drying in the air for several days assumed a pink tinge and appeared to effloresce. A sample dried at 100° melted at 192°, and its aqueous solution gave a violet coloration with ferric chloride:

0.1288 gave 0.2355 CO<sub>2</sub> and 0.0681 H<sub>2</sub>O. C=49.87; H=5.89.

C<sub>9</sub>H<sub>12</sub>O<sub>6</sub> requires C=50.0; H=5.6 per cent.

0.2451, on heating at 100° for two hours, lost 0.0203. H<sub>2</sub>O=8.0.

C<sub>9</sub>H<sub>10</sub>O<sub>5</sub>·H<sub>2</sub>O requires H<sub>2</sub>O=8.3 per cent.

On treatment with *p*-nitrophenylhydrazine in dilute acetic acid solution, a pale yellow, flocculent precipitate was obtained, which rapidly darkened in colour, finally assuming a chocolate-brown, and it was apparent that oxidation had taken place. The hydrazone was not obtained in a condition of sufficient purity for a melting-point determination or analysis.

Methylation of the above trihydroxy-compound with methyl sulphate gave  $\omega$ -2:4:6-tetramethoxyacetophenone, which has been described by Herzig and Hofmann (*Ber.*, 1909, **42**, 155), who obtained it by methylating 6-hydroxy- $\omega$ -2:4-trimethoxyacetophenone, the latter being isolated as a decomposition product from the action of alcoholic potassium hydroxide on the pentamethyl ether of morin.

The trihydroxy-compound (1.5 grams) was dissolved in 20 c.c. of sodium hydroxide solution containing 2 grams (6 mols.) of sodium hydroxide, and 4.2 grams (3.5 mols.) of methyl sulphate were added with vigorous stirring, rise in temperature being avoided. An oil soon separated, and, on cooling in ice-water, solidified to a pasty, crystalline mass, which was well drained. After crystallisation from methyl alcohol, the pure substance melted at 50°, and gave no coloration with ferric chloride (Found: C=59.86; H=6.81. C<sub>12</sub>H<sub>16</sub>O<sub>5</sub> requires C=60.0; H=6.66 per cent.).

*3:5-Dihydroxycumaran-2-one (VII).*

This substance has already been described by Soun (*Ber.*, 1917, 50, 1265). As previously stated, the same substance was prepared by the condensation of anhydrous phloroglucinol with hydroxy-acetonitrile. The ketimine hydrochloride which separated during the reaction was dissolved in water, and the solution warmed on the water-bath for half an hour. On cooling the red-coloured solution, crystals soon deposited, which, after being collected and washed with a little light petroleum, were only faintly red, and on crystallisation from hot water the pure substance was obtained in colourless plates, melting at  $248^{\circ}$  to a dark red liquid. An aqueous solution of the substance gave a purple coloration with ferric chloride.

The diacetyl compound was prepared by treating the substance with a few drops of pyridine, and then adding a slight excess of acetyl chloride. The mixture was warmed on the water-bath for one minute and then treated with water, and the oil which separated soon solidified. After crystallising the solid from methyl alcohol, it melted at  $122^{\circ}$ , and consisted of small, prismatic needles.

*5-Hydroxy-1-methylcumaran-2-one (IX).*

Resorcinol (5.6 grams:1 mol.) was dissolved in dry ether (25 c.c.), acetaldehydecyanohydrin (3.3 grams:1 mol.) added, and a current of dry hydrogen chloride passed into the solution for three hours. The ketimine hydrochloride separated during the process, and the quantity was increased by allowing the mixture to remain in a refrigerator for several days. The pale red, crystalline mass (about 8.5 grams) was dissolved in ice-water, and the solution carefully neutralised with solid sodium hydrogen carbonate, when the ketimine was precipitated as a pale yellow solid (6 grams):

0.1490 gave 10.4 c.c.  $N_2$  (moist) at  $18^{\circ}$  and 750 mm.  $N=8.15$ .

$C_9H_8O_2N$  requires  $N=8.58$  per cent.

The ketimine was soluble in water or sodium hydroxide solution on warming, and in both cases the solutions became deep red, and ammonia was simultaneously evolved. The aqueous solution, on cooling, deposited a straw-coloured, crystalline powder, which proved to be 5-hydroxy-1-methylcumaran-2-one. The base is soluble in hot methyl or ethyl alcohols, and crystallises from the latter in faintly yellow, small prisms melting at  $152^{\circ}$ . It is insoluble in benzene and sparingly soluble in ethyl acetate or acetone. Attempts to prepare a platinum salt were not successful, and resulted in the formation of tarry material, probably caused by oxidation.

The aqueous solution reduces Fehling's solution and Tollens's reagent.

As stated above, on boiling the aqueous solution of the ketimine, the corresponding cumaranone derivative was obtained, which crystallised from hot alcohol in prisms. The latter are sparingly soluble in hot water, soluble in sodium hydroxide solution, giving a yellow coloration, and also in hydrochloric acid, producing a deep red colour. The substance begins to decompose at 233° and melts and decomposes completely at 238—240°.

The aqueous solution of the cumaranone reduces silver nitrate solution, with the deposition of a silver mirror, and Fehling's solution is reduced on gentle warming, a precipitate of cuprous oxide being produced:

0.1160 gave 0.2800 CO<sub>2</sub> and 0.0514 H<sub>2</sub>O. C=65.80; H=4.92.

C<sub>9</sub>H<sub>8</sub>O<sub>3</sub> requires C=65.85; H=4.87 per cent.

Methylation of the above compound with methyl sulphate was unsuccessful, and resulted in the formation of a dark-coloured oil, which was difficult to purify.

#### 5-Methoxy-1-methylcumaran-2-one (XIII).

Auwers and Müller (*Ber.*, 1917, 50, 1172) have already described the properties of this compound, but the following method of preparation of it is different from that employed by these investigators. Resorcinol monomethyl ether (2.5 grams:1 mol.) and acetaldehydecyanohydrin (1.5 grams:1 mol.) were treated with hydrogen chloride in dry ethereal solution. At the end of an hour, 0.5 gram of zinc chloride was added, and the mixture allowed to remain at the ordinary temperature for two days. A red oil separated from the ether, and the latter was then decanted and the oil washed several times with small quantities of dry ether. On pouring into water, a clear solution was obtained, which, however, became cloudy on warming and a colourless oil separated. This solidified on cooling, and the solid crystallised from methyl alcohol in long, thin needles melting at 60°.

The present investigation is being continued on similar lines, and in concluding this paper we desire to thank Prof. Lapworth for the interest he has taken in the work, and also for placing various materials at our disposal.

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[Received, February 6th, 1920.]

### XXXIX.—*The Effect of Heating on the Absorptive Power of Sugar-charcoal for Sulphur Dioxide.*

By RAMSAY MIDDLETON WINTER and HERBERT BRERETON BAKER.

DURING the later stages of the war the absorptive power of charcoal for poisonous gases and lachrymatory vapours was of the greatest importance. In the earlier types of box respirators animal-charcoal was employed, but when the use of this type of respirator was extended to all troops, it became necessary to investigate other kinds of charcoal, of which an unlimited amount would be available. Experiments carried on at the Imperial College, chiefly by Prof. Philip, showed that, contrary to the earlier belief, wood-charcoal which had been subjected to long-continued heating gained so much in absorptive power that, in this respect, it was in no way inferior to animal-charcoal.

It was thought worth while to investigate this question further, using the purest charcoal obtainable, and incidentally to find out whether this increase in absorptive power was associated with any other changes in the physical properties of the charcoal.

The sugar-charcoal was prepared by heating the finest crystallised sugar until no fumes or odour were perceptible. After roughly powdering the mass, it was placed in a hard-glass flask, in which it was heated in a vacuum. Chlorine was then admitted and allowed to remain all night. The flask was next heated to redness for half an hour, a vacuum being maintained in it by means of a good water-pump. The charcoal on boiling with water gave no indication of the presence of chlorine or hydrochloric acid. It was heated in a muffle furnace for half an hour, powdered, and sieved. The particles between 0.4 and 0.8 mm. in diameter were used in the experiments.

The ash from different samples showed a very uniform percentage, 0.113 being the mean value.

*Specific Gravity of the Charcoal.*—The material which had been heated to about 900° in a muffle furnace for four hours had a specific gravity of 1.76, mean of six samples.

That which had been heated for forty hours had a specific gravity of 1.84, mean of two samples.

*Absorptive Power of the Charcoal.*—Sulphur dioxide was chosen for the first experiments, since the gas is easily obtained in a fairly pure state from the liquefied substance, and also because the amount absorbed is very considerable.

The gas was contained in a gas-burette over mercury, which, with its accompanying barometer tube, was surrounded by a jacket



through which water at a constant temperature was circulated. Sealed on to its exit-tube a long capillary tube communicated, by means of a mercury-protected ground joint, with the thick hard-glass bulb in which the charcoal was placed. It was found impossible to weigh the charcoal in an open weighing tube, so rapid was its absorption of water vapour from the air. No lubricator was used for the ground joint. By means of a screw clamp on each side the parts of the joint were kept in close contact, and no leakage occurred when, as sometimes happened, there was a considerable internal pressure. Before admitting the sulphur dioxide, the bulb containing the weighed charcoal was exhausted by means of a Gaede pump, and heated to redness for two hours. It was then cooled in a bath containing melting ice, the same water, at 0°, being circulated through the jacket of the gas-burette. The latter, which had a volume of about 100 c.c., had been carefully calibrated, and the volume of the bulb had been determined by weighing its volume of mercury. It was feared that the volume of the bulb might change on heating when exhausted. This was not found to be the case when the bulb was of sufficient thickness.

On admission of the sulphur dioxide the absorption was very rapid for the first hour. It then became extremely slow, but in seventy-two hours no further absorption could be measured. The results obtained were, with 1 gram of charcoal which had been heated previously for the times stated:

Hours .....	4	40	42½	45½
C.c. ....	97	195	241	288

Saussure (*Ann. Physik.* [Gilbert], 1814, **47**, 113) found that one volume of charcoal of sp. gr. 1.57 absorbed sixty-five volumes of sulphur dioxide, or 1 gram of charcoal absorbed 38 c.c. of sulphur dioxide.

Favre (*Ann. Chim. Phys.*, 1871, [iv], **24**, 247), with charcoal of the same specific gravity, found that 1 gram absorbed 105 c.c. of the gas.

#### Conclusion.

Charcoal, in a very pure form, has its specific gravity increased by forty hours' heating to 900° from 1.76 to 1.84. By the same treatment the amount of sulphur dioxide absorbed is increased from 97 c.c. to 288 c.c.

It is proposed to extend this investigation to the cases of other gases, and also to find if other physical properties of charcoal are affected by prolonged heating.

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LONDON.

[Received, March 3rd, 1920.]

## Organic Chemistry.

**Oxidation of Methane.** R. K. BAILEY (U.S. Pat. 1319748).

—Methane or natural gas is mixed with twice its volume of nitric oxide and with sufficient oxygen or air to form nitrogen peroxide. This mixture is passed through a porcelain or other inert tube heated to redness. Oxidation products, including formaldehyde, are obtained. The oxidation is prevented from being carried too far by conducting the reaction products as quickly as possible into a cooling chamber, where they are brought into contact with a sludge of calcium carbonate, which unites with the oxides of nitrogen, except nitric oxide. Formaldehyde is recovered from the solution after separating the solids from the sludge. Instead of using calcium carbonate, the hot reaction gases may be brought into contact with calcium oxide to effect absorption of water, thus preventing formation of nitrous and nitric acids, which if present would oxidise the formaldehyde. Reaction temperatures as low as 450° may be employed.

CHEMICAL ABSTRACTS.

**Methyl Sulphate.** T. H. DURRANS (U.S. Pat. 1317648).—

Methyl sulphate is produced, together with methyl hydrogen sulphate and methyl chloride, by treating methyl alcohol, preferably with cooling, with chlorine and sulphur dioxide, the latter preferably being in slight excess throughout the reaction. Methyl chloride is removed by distillation at the ordinary pressure and the methyl sulphate under reduced pressure, or the products may be used together as alkylating agents.

CHEMICAL ABSTRACTS.

**Improvements in the Manufacture of Aliphatic Nitrites.**

PAUL RENE DE WILDE (Brit. Pat. 133304).—Nitrites of aliphatic alcohols are produced by the reducing action of sulphur dioxide on solutions of the alcohols in pure or diluted nitric acid, or, alternatively, a saturated alcoholic solution of sulphur dioxide may be mixed with nitric acid. As an example, 74 grams of *isobutyl* alcohol dissolved in 100 grams of nitric acid (D 1.375) yield on treatment with sulphur dioxide 85 grams of *isobutyl* nitrite.

G. F. M.

**Preparation of Chloromethyl Carbonates.** ANDRÉ KLING,

D. FLORENTIN, and E. JACOB (*Compt. rend.*, 1920, 170, 111—113. Compare this vol., i, 139, and Grignard, Rivat, and Urbain, this vol., i, 139).—By the successive chlorination of methyl carbonate, mono-, di-, tri-, tetra-, penta-, and hexa-chloro-derivatives are obtained, the most symmetrical derivative being obtained in each case.

W. G.

**Properties of the Chloromethyl Carbonates.** ANDRÉ

KLING, D. FLORENTIN, and E. JACOB (*Compt. rend.*, 1920, 170, 234—236).—The physical properties of the nine possible chlorinated

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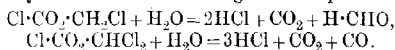
methyl carbonates, the preparations of which have previously been described (preceding abstract), are given, as below:

Formula.	M. p.	B. p./760 mm.	B. p./50 mm.	D <sub>4</sub>
CH <sub>3</sub> Cl·O·CO <sub>2</sub> Me ...	—	139—140°	67°	1.303
CO(O·CH <sub>2</sub> Cl) <sub>2</sub> ...	—	176°	99°	1.480
CHCl <sub>2</sub> ·O·CO <sub>2</sub> Me ...	—	147°	72°	1.421
CHCl <sub>2</sub> ·O·CO <sub>2</sub> ·CH <sub>2</sub> Cl	—	178°	102°	1.562
CCl <sub>3</sub> ·O·CO <sub>2</sub> Me ...	— 70° (viscous)	165°	86°	1.535
CO(O·CHCl <sub>2</sub> ) <sub>2</sub> ...	— 40°	182—183°	105—106°	1.618
CCl <sub>3</sub> ·O·CO <sub>2</sub> ·CH <sub>2</sub> Cl ...	— 70° (viscous)	150° (decomp.)	110°	1.631
CCl <sub>3</sub> ·O·CO <sub>2</sub> ·CHCl <sub>2</sub> ...	— 30°	196°	115°	1.686
CO(O·CCl <sub>3</sub> ) <sub>2</sub> ...	78°	203°	124°	—

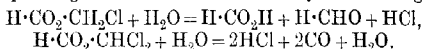
The substances which contain the group ·O·CCl<sub>3</sub> are particularly toxic.  
W. G.

**Organic Derivatives of Tellurium. I. Dimethyltelluronium Dihaloids.** RICHARD HENRY VERNON (T., 1920, 117, 86—98).

**The Industrial Chloromethyl Formates and their Analysis.** MARCEL DELÉPINE (*Bull. Soc. chim.*, 1920, [iv], 27, 39—45).—The mono- and di-chloromethyl chloroformates are decomposed by dilute alkali according to the equations:



The corresponding mono- and di-chloromethyl formates give



The formaldehyde formed may be estimated by Romijn's method (compare A., 1897, ii, 166), the formic acid by Péan de St. Gilles's method (compare *Ann. Chim. Phys.*, 1859, 55, 374), and the carbon monoxide by direct measurement of its volume after decomposing the material with sodium hydroxide. These results, together with the percentage of chlorine, enable an idea to be formed as to the different esters present in industrial chlorinated methyl formates. [See, further, *J. Soc. Chem. Ind.*, 1920, 205A.] W. G.

**Manufacture of Esters of Ethylenic Halogenhydrins.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat. 128911).—Ethylenic halogenhydrin esters of the general formula



where R is an alkyl or aryl group and X a halogen, are prepared by the interaction of ethylene oxide and an acetyl haloid in equimolecular proportions at a suitable temperature, depending on the particular acid chloride or bromide used. The reaction is conveniently brought about by passing gaseous ethylene oxide through the acetyl haloid at ordinary atmospheric pressure, and quantitative yields are obtained. Examples are given of the preparation of *β*-chloroethyl acetate, b. p. 143—144°, from acetyl chloride at its boiling point, *β*-chloroethyl chloroacetate, b. p. 94—95°/12 mm,

from chloroacetyl chloride at 100°, *β*-chloroethyl benzoate, b. p. 120—122°/5 mm., from benzoyl chloride at 190—240°, *β*-chloroethyl *p*-nitrobenzoate, yellow crystals, m. p. 56°, from *p*-nitrobenzoyl chloride at 190—240°, and *β*-bromoethyl acetate, b. p. 163°, from a mixture of equimolecular proportions of ethylene oxide and acetyl bromide kept for several hours at the ordinary temperature.

G. F. M.

**Colloid-chemical Studies on Soaps. Non-aqueous Lyophilic Soap Colloids.**

MARTIN H. FISCHER (*Chem. Eng.*, 1919, 27, 184—193).—The solvation capacities of various sodium soaps of the acetic series were determined. One gram-mol. of sodium arachidate will take up 27.5 litres of ethyl alcohol and still form a non-synergetic gel. The capacity of the lower members of the series becomes less as the molecular weight of the soap decreases. When a given soap is employed with different alcohols, the solvation capacity increases as the molecular weight of the alcohol becomes greater. The author has elaborated his theory of lyophilic and lyophobic colloids. The theory of soap gels is also dealt with. According to this, soaps form (*A*) true solutions in a solvent at higher temperatures. On the other hand, (*D*), a gel, when the temperature is low, is a true solution of the solvent in the solvated soap. Between these two extremes there exist two stages, (*B*) solvated soap dispersed in the solvent, (*C*) dispersed solvent in the solvated soap. If the temperature of *A* is lowered, all these stages are obtained. This is also true when the temperature of *D* is raised. The ranges of temperature in which *B* or *C* exists are not necessarily the same when the temperature of *A* is being lowered as when the temperature of *D* is being raised, because of a hysteresis effect. There exists, therefore, a region of ambiguity which depends on the previous history of the system. Gelation capacity is for these reasons not synonymous with solvation capacity. The latter is the phenomenon generally known as swelling, which is a different process from liquefaction.

CHEMICAL ABSTRACTS.

**Colloid-chemical Studies on Soaps.** MARTIN H. FISCHER and MARION O. HOOKER (*Chem. Eng.*, 1919, 27, 223—232. Compare preceding abstract.)—Solutions of sodium or potassium hydroxide of various concentrations are added to a standard aqueous solution of potassium oleate having the consistency of a syrup. As the concentration of the base is increased, the viscosity becomes greater until a gel is formed. Further addition of the base causes the soap to separate and the viscosity to fall rapidly. The separation of the soap occurs at a lower concentration for sodium hydroxide than for potassium hydroxide. The addition of aqueous ammonia always lowers the viscosity, the authors' explanation being that ammonium soaps are more soluble in water and are better solvents for water. Similar results are obtained when a sodium or potassium salt is added in place of the hydroxide, except that potassium acetate has a much greater salting-out effect than the chloride, nitrate, etc. Ammonium salts, on the other hand, emulsify the

soap, but do not salt it out. Calcium or magnesium salts form insoluble or less hydrated soaps, and therefore the viscosity steadily decreases as more of the salt is added. Salts of the heavy metals, such as copper or iron, cause the soap to separate in hard lumps. The effect is additive when potassium hydroxide or a potassium salt is also added.

CHEMICAL ABSTRACTS.

**Oleates and Stearates of certain Metals.** MATHEUS D'ANDRADE ALBUQUERQUE (*Revista Chim. pura appl.*, 1916, [ii], 1, reprint, 8 pp.).—The oleates and stearates of a number of metals were prepared by double decomposition of solutions of their salts with alkali soaps. The ethereal solutions of some of the metallic soaps oxidised on exposure to air; the action of hydrogen peroxide on the ethereal solutions was also ascertained.

Metal.	Colour of ethereal solution.	Oxidation by air to—	Oxidation by $H_2O_2$ to—	Stability of peroxidised solution.
Ag'	colourless	—	pale yellow	—
Cu'	amber-yellow	bluish-green	—	—
Cu''	bluish-green	—	yellowish-brown	unstable
Hg'	colourless	—	no colour change	—
Hg''	colourless	—	no change	—
Mn''	almost colourless	—	dark chestnut	stable
Co''	red	dark green	dark green	stable
Pb''	colourless	—	orange-yellow	very unstable
Cr'	pink	violet	violet	—
Cr'''	violet	—	no change	—
V''	violet (?)	green (at once)	not given	—

Titanium soaps could not be obtained. The cuprous compounds were made from cupric soaps by reduction with hydrazine sulphate as well as by the action of alkali stearate and oleate on moist cuprous chloride. The silver compounds were darkened by light. By means of the ethereal soap solutions, it was possible to observe the absorption spectra of the various metals in the non-ionised state. The chromic compounds showed a strong absorption in the yellow.

W. R. S.

**[Preparation of] Maleic Acid from Benzoquinone by Catalytic Oxidation.** J. M. WEISS and C. R. DOWNS (U.S. Pat. 1318632).—Maleic acid is produced by dissolving benzoquinone in benzene and subjecting the mixture in the vapour phase to catalytic oxidation under conditions as described in U.S. Pat. 1318631 (this vol., i, 236). Inert diluent gases may be employed to control the reaction. In the condensate obtained from the reaction product there is usually present benzoquinone, maleic acid, benzene, formaldehyde, water, and various other by-products.

CHEMICAL ABSTRACTS.

**[Preparation of] Maleic Acid by Catalytic Oxidation of Benzene.** J. M. WEISS and C. R. DOWNS (U.S. Pat. 1318633).—The patent relates to a method of the same character as the described above (preceding abstract), preferably operating at 300–550°, with subsequent recovery of maleic acid as the main

product. When equal weights of benzene vapour and air are passed over vanadium oxide as a catalyst at such a velocity that the mixture stays in contact with the catalyst about 0.25 sec., a maximum yield of maleic acid is obtained by maintaining the catalyst at 400—450°.

CHEMICAL ABSTRACTS.

**The Mode of Pyrogenic Decomposition at High Temperature of Acetaldehyde, Metacetaldehyde, and Ethyl Alcohol.** (MLLZ.) EGLANTINE PEYTRAL (*Bull. Soc. chim.*, 1920, [iv], 27, 34—39).—When acetaldehyde is submitted to a high temperature for a very short time, the main decomposition is its conversion into carbon monoxide and methane, the molecule thus undergoing the least deformation possible. A second reaction proceeding at the same time, but to a less extent, yields carbon monoxide, ethylene, and oxygen. If the time of heating is prolonged, other secondary products, such as acetylene and benzene, appear.

Metacetaldehyde, under similar conditions, is first depolymerised to give acetaldehyde, which then undergoes the changes given above. In the case of ethyl alcohol, the principal reaction is its oxidation to acetaldehyde, which then undergoes pyrogenic decomposition, as described. A second reaction proceeding simultaneously, but to a lesser extent, results in the conversion of the alcohol into ethylene and water.

W. G.

**A Keto-glycol Derived from Mesityl Oxide.** J. PASTUREAU and CH. LAUNAY (*Bull. Soc. chim.*, 1919, [iv], 25, 593—597).—The crystalline compound, m. p. 123°, obtained by Wolfenstein (compare A., 1895, i, 644) by the action of hydrogen peroxide on mesityl oxide, is shown to be not a glycol, as described by him, but a peroxide of mesityl oxide,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \end{smallmatrix} \cdot \text{O} \begin{smallmatrix} \diagup \quad \diagdown \\ \text{C} \quad \text{C} \end{smallmatrix} \cdot \text{O}$ , and on hydrolysis it loses oxygen and gives the glycol of mesityl oxide described by Harries and Pappos (compare A., 1901, i, 673).

W. G.

**Lactose.** J. GILLIS (*Rec. trav. chim.*, 1920, 39, 88—125).—A more detailed account of work already published (compare A., 1918, i, 101, 155).

W. G.

**Lignin.** ERIK HÄGGLUND (*Arkiv. Kem. Min. Geol.*, 1918—1919, 7, No. 8, 1—20).—Reviewing the results of previous workers, the author attaches most importance to those of Klason (A., 1908, i, 717, and *Svensk Papperstidning*, 1916, No. 17), derived from a study of the ligninsulphonic acids; but the regeneration of lignin from these derivatives by means of 70% sulphuric acid, a method also used by Koenig (*Chem. Zeit.*, 1912, 36, 1101), requires one to two hours, and is accompanied by considerable decomposition of the lignin. The author now finds that 28% by weight of the wood of "hydrochloric acid-lignin" is obtained by shaking 1 part of finely powdered pine wood with 10 parts of 43% hydrochloric acid for fifteen minutes, rapidly filtering, and washing the residue free from hydrochloric acid. The product is a

pale brown powder with a strong odour of vanillin, and contains 1.63% of combined chlorine. It gives a deep purple colour with phloroglucinol in hydrochloric acid solution, a pale yellow colour with aniline sulphate, a dark red colour with *p*-phenylenedimethyldiamine sulphate, a dark blue colour with equal parts of potassium ferricyanide and ferric chloride, but no precipitate with Maule's reagent. A comparison of its methoxyl content with that of the original wood shows that about 20% of this is split off during the hydrochloric acid treatment. After introducing a corresponding correction, the author's analytical results agree with Klason's formula,  $(C_{20}H_{40}O_{11})_n$ , for lignin, but not with those of Cross and Bevan ("Cellulose," iii) or of Green (Schwalbe, "Chemie der Cellulose," 1911, 448). Protocatechuic acid was identified among the products of fusion of hydrochloric acid-lignin with potassium hydroxide and lead peroxide, but acetic acid, oxalic acid, and catechol could not be detected. The formation of these products from wood (Lange, A., 1890, 228) is therefore due to other constituents than lignin. The author also investigated his product in regard to its furfuraldehyde content, solubility in bisulphites and in alkalis, the action of chlorine and bromine, its oxidation with alkaline permanganate and with potassium chlorate and nitric acid, and the results of dry distillation. J. K.

**Salts of  $\beta$ -Hydroxytrimethylenediglycine and of *N*-Hydroxymethylglycine.** HUGO KRAUSE (*Ber.*, 1919, 52, [B], 1211—1222).

The peculiarity (A., 1918, i, 156) attending the formation of the barium salt ( $+3H_2O$ ) of  $\beta$ -hydroxytrimethylenediglycine (the barium salt containing  $1.5H_2O$  [A., 1918, i, 337] is now stated to be non-existent) has been examined. It is due to supersaturation, which, however, is not always operative; in many experiments a noteworthy retardation of the crystallisation was never observed when technical formalin reacted with a freshly prepared solution of barium glycine or when a solution of the latter which had been kept in the cold for an hour or longer was treated with formaldehyde solution containing or not containing methyl alcohol. The initiation of crystallisation by the addition of a little methyl alcohol (*loc. cit.*) cannot be regarded, therefore, as a proof that the alcohol plays a part in the reaction.

A second barium salt of the same composition,



which is amorphous and extremely soluble in water, is obtained by treating a 25% solution of  $\beta$ -hydroxytrimethylenediglycine in formalin, which has been kept for a few days, with the theoretical quantity of a 15% paste of barium hydroxide, and adding 8 vols. of 80% methyl alcohol to the resulting, almost clear solution.

Some experiments on the simultaneous formation of the barium salts of  $\beta$ -hydroxytrimethylenediglycine and *N*-hydroxymethylglycine indicate that the production of the latter is favoured by working at low temperatures with pure formaldehyde, any considerable excess of which is to be avoided.

In addition to the salts of *N*-hydroxymethylglycine already described (*loc. cit.*; A., 1919, i, 67), the following have been prepared by the action of pure 33% formaldehyde solution on the metallic glycine salt: *potassium*,  $\text{OH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$ , amorphous, brittle mass, which is obtained in a purer form by treating the normal lead salt with potassium sulphide; *sodium* (at 80° in a vacuum these two salts [2 mols.] appear to lose water [1 mol.], with the formation of anhydro-salts); *barium* (+ 2H<sub>2</sub>O), microscopic rods; *calcium* (+ 1H<sub>2</sub>O), hygroscopic, amorphous powder. The copper and lead salts must be dried over calcium chloride, not over sulphuric acid (*loc. cit.*), which causes loss, not only of water, but also of a little formaldehyde. C. S.

**Behaviour of Carbamide towards Hydrogen Peroxide and a Simple Process for its Purification and Decoloration.**

HERMANN KUNZ-KRAUSE (*Kolloid Zeitsch.*, 1919, 25, 240—241).—Carbamide is not affected in the slightest degree by boiling it in aqueous solution with hydrogen peroxide, but colloidal colouring matter, which is generally present in carbamide, is destroyed. Carbamide made from potassium cyanide which has been obtained from potassium ferrocyanide often exhibits a blue to green tint, which cannot be removed by recrystallisation. The colour is due to Prussian-blue, and is destroyed by boiling the carbamide with hydrogen peroxide. J. F. S.

**Carboalkyloxythiocarbamides.** AUGUSTUS EDWARD DIXON and RAYMOND THOMAS JOACHIM KENNEDY (T., 1920, 117, 80—85).

**Preparation and Separation of Cyanates Soluble in Water.** J. D. RIEDEL (D.R.-P. 314629; from *Chem. Zentr.*, 1919, iv, 913).—Chlorine or bromine is directly added to highly concentrated alkaline solutions of cyanides; formation of cyanogen haloid only occurs to a subsidiary extent. Sodium cyanate is smoothly formed by this reaction, and is deposited in the solid state from its solution as the process goes forward. The product is applicable to technical and pharmaceutical purposes. H. W.

**Free Thiocyanogen.** ERIK SÖDERBÄCK (*Annalen*, 1919, 419, 217—322).—The author discusses the unsuccessful attempts of Liebig (1829 and 1844), Linnemann (1861), and Schneider (1866) to prepare thiocyanogen. Klason's compound,  $(\text{CN})_3\text{S}_3\cdot\text{S}_3(\text{CN})_3$ , obtained in 1886, is a cyanuric derivative. Quite recently, Bjerrum and Kirschner have detected small quantities of thiocyanogen in aqueous solutions of complex gold thiocyanates,  $\text{MAu}(\text{SCN})_4$ .

When an ethereal *N*- or *N*/10-solution of iodine is shaken with silver thiocyanate in excess, the colour of the iodine rapidly fades and yellow silver iodide is formed. The reaction, however, appears to reach a state of equilibrium. As it is impossible to separate completely the excess of iodine from the soluble product of the



reaction, the halogen is removed as far as possible by mercury and the pale yellowish-brown solution examined. As the author expected it to be a dilute solution of thiocyanogen and to behave analogously to the halogens, it was treated with (1) chlorides and bromides, whereby no appreciable effect was produced; (2) aqueous or alcoholic solutions of iodides (of cadmium, lead, silver, and mercury), whereby iodine was liberated; (3) iron powder, whereby ferric thiocyanate was produced in such quantity that the solution became opaque; (4) mercury, whereby mercurous thiocyanate was formed; (5) cuprous thiocyanate, whereby black cupric thiocyanate was formed; and (6) water, which slowly decomposed the thiocyanogen producing thiocyanic acid, hydrogen cyanide, and sulphuric acid.

The solvent ether can be replaced by acetone, absolute ethyl alcohol, chloroform, carbon tetrachloride, benzene, ethylene dibromide, or carbon disulphide. The reaction proceeds very slowly in the last solvent, but almost reaches completion in chloroform; in every case, however, a state of equilibrium appears to be attained.

The thiocyanates of potassium, zinc, cadmium, copper, and lead do not react appreciably with a solution of iodine, but mercuric thiocyanate reacts in the same way as silver thiocyanate.

Much better results are obtained with bromine. A solution of bromine in dry ethyl ether, ethyl chloride, ethyl bromide, carbon disulphide, carbon tetrachloride, chloroform, benzene, or ethylene dibromide reacts completely with the thiocyanates of silver, lead, cadmium, mercury, zinc, thallium, and copper in accordance with the equation  $2\text{MSCN} + \text{Br}_2 = 2\text{MBr} + 2\text{CNS}$ , since the resulting solution (in carbon disulphide or tetrachloride) is completely free from bromine, and in experiments with silver, lead, and mercury thiocyanates in which an excess of bromine was used, the solid product of the reaction is the pure metallic bromide. The velocity of the reaction is influenced by the solvent. A *N*-solution of bromine in carbon disulphide is decolorised by lead thiocyanate in slight excess within a few minutes, whilst about half an hour is necessary when the solvent is dry ether. A solution of bromine in carbon disulphide dried with phosphoric oxide is not decolorised by lead thiocyanate after one hour, but is almost instantly decolorised by silver or mercury thiocyanate.

The solutions of thiocyanogen obtained above are usually faintly yellow, but are occasionally quite colourless. The more concentrated solutions have a stinking odour resembling that of thiocyanic acid, and stain the skin pale red, changing to yellow. The solutions become turbid on keeping and deposit yellow or yellowish-red amorphous products. The decomposition proceeds slowly in ethyl chloride or bromide or ether, and very rapidly in carbon disulphide. The amorphous products, which are different from different solvents, appear to be mixtures consisting chiefly of polythiocyanogen. ( $\text{CNS}$ ),: about 1% of hydrogen is also present.

Chlorine in carbon tetrachloride solution does not react with lead thiocyanate, but yields a solution of thiocyanogen and the corre-

sponding metallic chloride by shaking with an excess of silver or mercury thiocyanate; sulphur chloride and cyanogen chloride are not present in appreciable quantities in the resulting solution.

The author's usual practice for the preparation of a solution of thiocyanogen is to treat lead thiocyanate with a dry ethereal solution of bromine cooled by ice-water.

The evaporation in a vacuum over sulphuric acid of an approximately  $N/2$ -solution of thiocyanogen in ethyl chloride, bromide, or ether left a clear, viscous, unstable, yellow oil. By cooling an approximately  $N/2$ -solution in carbon disulphide to  $-70^{\circ}$ , *thiocyanogen*, CNS, is obtained in cruciform aggregates of almost colourless crystals, m. p.  $-3^{\circ}$  to  $-2^{\circ}$ . The molten substance can be supercooled to  $-20^{\circ}$ , but always resolidifies at  $-30^{\circ}$ , giving well-defined rhombic plates. By allowing it to warm to the ordinary temperature, thiocyanogen becomes reddish-brown and more viscous; finally, a yellow smoke is evolved and a dark brick red, amorphous solid is formed. Thiocyanogen dissolves extremely rapidly in ethyl alcohol or ether, but only slowly in carbon disulphide or tetrachloride. Thiocyanogen is at least as strongly electronegative as iodine.

A solution of thiocyanogen reacts with zinc and cadmium (solvent, carbon disulphide mixed with about one-fifth the volume of absolute ethyl alcohol) to form the respective thiocyanates; with mercury (solvent, carbon tetrachloride) to form mercurous thiocyanate; with aluminium (solvent, dry ether) to form an *etherate* of aluminium thiocyanate,  $Al(SCN)_3 \cdot 2Et_2O$ , extremely hygroscopic, colourless plates, which become friable, and ultimately a syrup in air; with tin (solvent, carbon disulphide mixed with a small quantity of dry ether) to form an *etherate* of stannic thiocyanate,  $Sn(SCN)_4 \cdot 2Et_2O$ , yellow, apparently prismatic, hygroscopic crystals, which change into a syrup in air; with arsenic (solvent, carbon disulphide) to form *arsenious thiocyanate*,  $As(SCN)_3$ , almost colourless crystals; with antimony (solvent, dry ether) to form an extremely hygroscopic antimony thiocyanate (not isolated); with an excess of iron (ferrum reductum) (solvent, dry ether) to form ferrous thiocyanate, and with a deficit of iron to form anhydrous ferric thiocyanate, dark violet, crystalline powder; with manganese (solvent, ether and alcohol) to form manganous thiocyanate; with nickel (solvent, carbon tetrachloride), cobalt (solvent, carbon disulphide and alcohol), and silver (solvent, ether) to form the respective metallic thiocyanates, and with gold (solvent, none) to form, apparently, a mixture of aurous and auric thiocyanates (not isolated). Many of the experiments with metals are of a qualitative nature only.

The molecular weight of thiocyanogen cannot yet be determined. It does not yield well-defined products by treatment with organo-magnesium compounds. In order to ascertain which of its three atoms is the reactive one, a solution in dry ether was treated with mercury diphenyl, whereby phenyl thiocyanate and phenyl mercurithiocyanate,  $Ph \cdot Hg(SCN)$ , m. p.  $231-232.5^{\circ}$  (Otto in 1870 gave m. p.  $226-227^{\circ}$ ), were obtained: the latter was also obtained from

phenyl mercuri-iodide and thiocyanogen in carbon disulphide solution. Ethereal solutions of thiocyanogen and zinc ethyl react to form zinc thiocyanate and ethyl thiocyanate.

Thiocyanogen in solution does not yield well-defined products with ammonia or aliphatic amines, but in cold ethereal solution it reacts with aniline in accordance with the equation  $2\text{PhNH}_2 + 2\text{CNS} = \text{NCS} \cdot \text{C}_6\text{H}_5 \cdot \text{NH}_2 + \text{PhNH}_2 \cdot \text{HSCN}$  to form aniline thiocyanate and *p*-thiocyanoaniline, colourless, odourless needles (from water), m. p. 57–57.5°. When twice the quantity of thiocyanogen is used, the product is *p*-thiocyanoaniline thiocyanate, faintly red crystals. By reduction with hydrochloric acid and zinc dust, *p*-thiocyanoaniline yields *p*-aminophenyl mercaptan, which was identified by oxidation to the corresponding disulphide. In a similar manner, thiocyanogen and dimethylaniline react in ethereal solution to form dimethylaniline thiocyanate and *p*-thiocyanodimethylaniline,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SCN}$ , colourless, odourless crystals, m. p. 73–74°, which yields *p*-dimethylaminophenyl mercaptan by reduction. Diphenylamine and thiocyanogen in ethereal solution yield thiocyanic acid and ? : ?-dithiocyanodiphenylamine,  $\text{NH}(\text{C}_6\text{H}_5)_2 \cdot \text{SCN}$ , faintly greenish-yellow needles, m. p. 120°, whilst triphenylamine under similar conditions yields thiocyanic acid and ? : ?-dithiocyanotriphenylamine, needles, m. p. 115–116°.

Phenol and thiocyanogen in carbon disulphide solution react to form thiocyanic acid (which was not detected, however, being apparently converted by a secondary reaction into an insoluble, yellowish-brown substance) and *p*-thiocyanophenol, colourless, odourless plates of rhombic habit, m. p. 53–54°, the constitution of which was proved by its conversion through *p*-hydroxyphenyl mercaptan into *pp'*-dihydroxydiphenyl disulphide, and also by its formation from *p*-thiocyanoaniline by the diazo-reaction.

Some experiments on the competition of iodine and thiocyanogen in solution for a metal show that the equilibrium  $\text{MSCN} + \text{I} \rightleftharpoons \text{MI} + \text{CNS}$  is largely dependent on the nature of the metal; in the case of cadmium, the reaction from right to left is practically irreversible.

Stannous thiocyanate, produced by the interaction of lead thiocyanate and stannous sulphate in aqueous solution, and obtained in colourless crystals from the hot filtrate after removing lead sulphate, is converted into the etherate of stannic thiocyanate by a solution of thiocyanogen in a mixture of carbon disulphide and ether.

An ethereal solution of thiocyanogen reacts with mercuric cyanide (and also with silver or zinc cyanide) to form mercuric thiocyanate and a substance which is identical with the cyanogen sulphide,  $(\text{CN})_2\text{S}$ , described by Linnemann and by Schneider; from this method of preparation, the substance might be cyanogen thiocyanate,  $\text{CN} \cdot \text{SCN}$ .

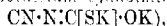
Several investigators have recorded the production of a very unstable, blood-red substance when a concentrated aqueous solution of potassium thiocyanate is acidified with sulphuric acid and treated

with a solution of sodium nitrite. This substance, which almost immediately decomposes, with the evolution of nitric oxide, can also be obtained by treating a solution of nitrosyl chloride in carbon tetrachloride with silver thiocyanate at the ordinary temperature. It appears to be *nitrosyl thiocyanate*,  $\text{NO}\cdot\text{SCN}$ , since its solution, which is relatively stable at  $-17^\circ$ , converts cuprous thiocyanate into cupric thiocyanate and metallic mercury into mercurous thiocyanate, and reacts with aqueous sodium hydroxide to form sodium thiocyanate and sodium nitrite. The author has performed some preliminary experiments in which the substance is produced from nitric oxide and thiocyanogen in well-cooled carbon disulphide. The substance allies itself with the nitrosyl haloids in its properties, its position falling between those of the bromide and iodide.

Although its molecular weight cannot yet be ascertained, the author is of opinion that the molecular magnitude and the constitution of thiocyanogen in solution are represented by the formula  $\text{CN}\cdot\text{S}\cdot\text{S}\cdot\text{CN}$ . In accordance with this nitrile structure, a dry ethereal solution of thiocyanogen reacts with dry ethereal hydrogen chloride cooled with ice-water to form a precipitate of a colourless, crystalline *substance*,  $2\text{CNS}\cdot 2\text{HCl}$  (which becomes yellow above  $100^\circ$  and changes gradually to a brown substance without melting), and a solution of a *substance*,  $2\text{CNS}\cdot 2\text{HCl}$ , pale yellow prisms or plates of rhombic habit, m. p.  $69-70^\circ$ . In contrast to the former, the latter substance, which is not formed when carbon disulphide, carbon tetrachloride, chloroform, or benzene is employed as solvent, is easily soluble in organic solvents and is unaffected by hot water. The substance,  $2\text{CNS}\cdot 2\text{HCl}$ , is converted by water into a *substance*, pale yellow, rhombic leaflets or needles, which decomposes without melting when heated, and has the composition of thiocyanogen hydrate,  $(\text{CNS})_2\cdot\text{H}_2\text{O}$ . The latter substance is regarded as 2-imino-

5-keto-1:3:4-dithiazolidine,  $\text{NH}\begin{smallmatrix} \text{CO} \text{---} \text{S} \\ \diagup \quad \diagdown \\ \text{C}(\text{NH}) \end{smallmatrix}$ , since it presents

several points of analogy to perthiocyanic acid (2-imino-5-thio-1:3:4-dithiazolidine; Hantzsch and Wolvekamp, A., 1904, i, 718), particularly in its behaviour with cold aqueous potassium hydroxide, whereby sulphur is liberated and a colourless, crystalline *substance*,  $\text{C}_2\text{ON}_2\text{SK}_2$  (*potassium cyanoiminodithiocarbonate*,



analogous to potassium dithiocyanate (cyanoiminodithiocarbonate), produced. The substance  $2\text{CNS}\cdot 2\text{HCl}$  is probably 5:5-dichloro-2-

imino-1:3:4-dithiazolidine,  $\text{NH}\begin{smallmatrix} \text{CCl}_2 \text{---} \text{S} \\ \diagup \quad \diagdown \\ \text{C}(\text{NH}) \end{smallmatrix}$ . When suspended in

benzene, it reacts with aniline to form the hydrated hydrochloride of Fromm's thiuret (A., 1893, i. 575).  $\text{C}_8\text{H}_7\text{N}_3\text{S}_2\cdot\text{HCl}\cdot 3\text{H}_2\text{O}$ .

C. S

### Photochemical Oxidation of Potassium Thiocyanate.

DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1919, 58, 457—463).—Under the influence of sunlight, aqueous potassium thiocyanate solutions undergo change, in which the atmospheric oxygen takes

part. With solutions of medium concentration, this change takes place with great rapidity, an amorphous, yellow precipitate of pseudocyanogen sulphide separating in most cases; if the concentration is either above or below a certain limiting value, the change is either entirely prevented or proceeds only very slowly. The concentration of the thiocyanate most favourable to the separation of pseudocyanogen sulphide is about 50% in the summer and about 10% in the winter. The purer potassium thiocyanates, especially those quite free from traces of ferrous salts, are more sensitive to this reaction than less pure preparations.

In addition to pseudocyanogen sulphide, the photochemical decomposition of potassium thiocyanate yields as constant products hydrocyanic and sulphuric acids, carbon dioxide, and ammonium salts,  $12\text{KCNS} + 12\text{O}_2 + 6\text{H}_2\text{O} = 6\text{K}_2\text{SO}_4 + 3\text{HCN} + 3\text{CO}_2 + 3\text{NH}_3 + 2(\text{CNS})_2$ . Further, there is always formed an unstable, intermediate peroxygenated compound, which imparts a blue colour to fresh guaiacum tincture, and is possibly analogous to Caro's acid.

Normal, decinormal, and centinormal solutions of potassium thiocyanate undergo these alterations, but only with the first of these does separation of pseudocyanogen sulphide take place. Although decomposed in this way, the deci- and centi-normal solutions show, within certain limits of time, no sensible diminution in titre, probably owing to the replacement, at least in the early stages of the change, of the thiocyanate by an equivalent proportion of the cyanide. T. H. P.

**Direct Passage from the Nitrous Esters and Nitro-compounds to Nitriles by Catalysis.** ALPH. MAILHE and (MME) M. L. BELLEGARDE (*Bull. Soc. chim.*, 1919, [iv], 25, 588—593).—By the catalytic hydrogenation of *isoamyl* nitrite by means of reduced nickel at  $280^\circ$ , primary, secondary, and tertiary amines result, with a small amount of *isovaleronitrile*. If the temperature of hydrogenation is increased to  $300\text{--}320^\circ$ , the yield of nitrile is considerably increased at the expense of the amines. At the same time, a certain amount of *isoamyl* alcohol is obtained, owing to hydrolysis of some of the nitrite, and a portion of the alcohol then undergoes dehydrogenation, giving the corresponding aldehyde. Similar results were obtained with propyl, *isobutyl*, and heptyl nitrites.

In the same way, at temperatures above  $300^\circ$ , nitromethane gave some hydrogen cyanide and nitropentane some *isovaleronitrile*.

W. G.

**Fixation of Nitrogen in the Form of Hydrogen Cyanide by means of an Electric Arc.** E. BRINER and A. BARRFUS (*Helv. Chim. Acta*, 1919, 2, 663—666).—Mixtures of hydrocarbons and nitrogen when submitted to the action of an electric arc produce hydrogen cyanide in yields much superior to the yield of ammonia obtained from nitrogen and hydrogen. The method employed is similar to that previously described (A., 1919, ii, 338).

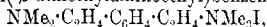
The mixture of gases circulates at the rate of 8–10 litres per hour in a chamber where an arc of 0.020 amp. is burning between platinum electrodes 7 mm. apart. Using 12 parts of methane, 23 of nitrogen, and 65 of hydrogen under 635 mm. pressure, 0.08% by volume of hydrogen cyanide is obtained. This gives a yield of 0.46 gram of hydrogen cyanide per kilowatt hour, in addition to a yield of 0.14 gram of ammonia per kilowatt hour. In this case, the *E.M.F.* applied was 1020 volts. With the same mixture, but with an *E.M.F.* of 420 volts, 0.12% by volume of hydrogen cyanide was obtained, which is 1.75 gram per *K.W.H.* and 0.44 gram of ammonia per *K.W.H.* The best case examined is with a mixture of 1 part of methane and 5 of nitrogen at 505 volts, where a yield of 0.75% by volume of hydrogen cyanide was obtained, which is 7.39 grams of hydrogen cyanide per *K.W.H.* and 0.48 gram of ammonia per *K.W.H.*

J. F. S.

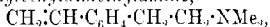
**Action of Carbon Monoxide on Sodium Alkyls.** WALTER SCHOELLER, WALTER SCHRAUTH, and WALTER ESSERS (*Ber.*, 1920, **53**, [B], 62–63).—In reference to Schlubach's communication on this subject (this vol., i, 19), reference is given to earlier work by the authors on the action of carbon monoxide on mercury acetate (*A.*, 1913, i, 1162).

J. C. W.

**Preparation of *o*-Divinylbenzene.** JULIUS VON BRAUN and LUDWIG NEUMANN (*Ber.*, 1920, **53**, [B], 109–113).—The pure methiodide of *o*-di-( $\beta$ -dimethylaminoethyl)benzene,



has m. p.  $196^\circ$ , and not  $175$ – $185^\circ$  as previously stated (*A.*, 1917, i, 130). When boiled with sodium hydroxide in a current of steam, the salt is decomposed into an amorphous, pale yellow polymeride of *o*-divinylbenzene,  $\text{C}_6\text{H}_4(\text{CH}:\text{CH}_2)_2$ , m. p.  $206$ – $207^\circ$ , and also  $\beta$ -*o*-vinylphenylethyldimethylamine,



which passes over in the steam. The base has b. p.  $123$ – $124^\circ/13$  mm., and forms a *picrate*, yellow leaflets, m. p.  $137^\circ$ , a *platinochloride*, m. p.  $167^\circ$ , and a silvery *methiodide*, m. p.  $209^\circ$ . The corresponding quaternary ammonium hydroxide is stable in solution, but yields the above polymeride on evaporation. Seeing that the isolated unsaturated base is so stable, it appears that the extensive decomposition which it suffers in the above reaction is "induced" by the decomposition of the other group. J. C. W.

**The Two Isomeric Diphenylindenes.** A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], **25**, 598–600).—The author shows that the diphenylindene obtained by him by the action of heat on  $\alpha\beta\gamma$ -triphenylpropene dibromide (compare *A.*, 1914, i, 265) is really the  $\alpha\beta$ -diphenylpropene, and that during the formation of its benzylidene derivative or its oximino-derivative it undergoes isomerisation to the  $\beta\gamma$ -diphenylindene described by Thiele and Ruggli (compare *A.*, 1912, i, 866).

W. G.

**Action of Light on I-10-Bromophenanthrene-3(or 6)-sulphonic Acid.** HÅKAN SANDQVIST (*Arkiv Kem. Min. Geol.*, 1917-18, 7, No. 4, 1-14).—In a previous paper (A., 1915, i, 795), the author has shown that the action of light on aqueous solutions of 10-bromophenanthrene-3(or 6)-sulphonic acid in hydrochloric acid decreases the viscosity of the solution, and has explained this as being due to the light changing an *a*-form of the acid into the *b*-form. Each form was supposed to give salts with different solubilities, water of crystallisation, etc., but the further experiments of the author with the barium salt have not led to the isolation of two such isomerides. However, from the more soluble fractions of the barium salt, which had been exposed to an intense light, a reddish-brown to black, varnish-like acid was obtained, which immediately lowered the viscosity of a sulphonic acid-hydrochloric acid mixture when added to it. From this dark acid, the dimethyl ester was prepared, and analysis showed it to be *dimethyl monobromodiphenanthryldisulphonate* (annexed formula); the barium salt was

$$\begin{array}{l} (7) \text{C}_{14}\text{H}_7 \begin{array}{l} \text{Br} \\ \diagup \quad \diagdown \\ \text{SO}_2\text{Me} \end{array} \text{ (3 or 6)} \\ (10') \text{C}_{14}\text{H}_8 - \text{SO}_2\text{Me} \text{ (3' or 6')} \end{array}$$

of 0.02% to the sulphonic acid-hydrochloric acid solution lowers the viscosity to one-third of its former value.

From the mother liquors of the above-mentioned barium salt another substance was isolated, but not identified, which lowered the viscosity, but not to such a great extent. Phenanthraquinone-3-sulphonic acid exerts a still less effect. The product formed, together with II-10-bromophenanthrene-3(or 6)-sulphonic acid in the bromination of phenanthrene-3-sulphonic acid (*ibid.*, 1917, 6, No. 13, 13) has exactly the same effect as the above-mentioned product of the action of light, and is therefore probably the same substance.

It is shown experimentally that the presence of monobromodiphenanthryldisulphonic acid or its barium salt accounts for the differences in solubility, etc., described in the previous paper (*loc. cit.*). T. S. P.

**Amine Oxidation. I. Oxidation of Aniline.** STEFAN GOLDSCHMIDT (*Ber.*, 1920, 53, [B], 28-44).—In Bamberger's interpretation of the oxidation of aniline, phenylhydroxylamine is regarded as the initial product. Whilst this compound may very well lead ultimately to nitrobenzene, it does not offer a satisfactory explanation of the formation of the polynuclear oxidation products, since it is not sufficiently reactive. It has been shown, however, that benzoquinonephenyldi-imine, which is regarded as the precursor of aniline-black, and azobenzene, are the first demonstrable products of the oxidation by alkaline permanganate or bleaching powder, whereas these are not formed under conditions appropriate to the production of phenylhydroxylamine, and ultimately nitro-

benzene. It appears, therefore, that there are two different initial products, varying according to the conditions. Agents which readily yield atomic oxygen, such as Caro's acid or hydrogen peroxide, produce aniline oxide, and further developments follow as in the scheme:  $\text{PhNH}_2 \rightarrow \text{PhNH}_2\text{:O} \rightarrow \text{PhNH-OH} \rightarrow \text{PhNO} \rightarrow \text{PhNO}_2$ , and  $\text{PhNO} + \text{PhNH-OH} \rightarrow \text{PhN} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{NPh} \end{array}$ , and

$\text{PhNO} + \text{PhNH}_2 \rightarrow \text{PhN:NPh}$ . Under other conditions, however, the initial stage is represented by the removal of two atoms of hydrogen, subsequent changes being due to the activity of the  $\text{PhN}\cdot$  residue (compare A., 1913, i, 1173). This radicle may, for example, polymerise to azobenzene, benzoquinonephenyldi-imine,  $\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{NH}$ , or emeraldine. This assumption is based on the fact that azo-compounds and quinonearyldi-imines can be isolated when aniline, and especially its nuclear-substituted methyl homologues having free para-positions, are oxidised by lead peroxide. The theory is considerably strengthened by the further fact that mixed azo-compounds and mixed quinonearyldi-imines are produced when two amines are oxidised together.

The methylated quinonearyldi-imines are easily hydrolysed by acids to the original amine and the quinone, and may thus be identified. They differ, therefore, from unsubstituted benzoquinonephenyldi-imine, which mainly polymerises to emeraldine. This explains, therefore, why Willstätter obtained only duroquinone in an attempt to oxidise aminodurene in acid solution to a methylated emeraldine (A., 1909, i, 899).

In the oxidation of aniline itself, the base is dissolved in ether and shaken with lead peroxide and anhydrous sodium sulphate. The filtered oxidation products are then shaken with alcohol, ammonium chloride, and zinc dust to reduce the benzoquinonephenyldi-imine to *p*-aminodiphenylamine. A current of steam removes unchanged aniline and azobenzene, whilst the diamine is isolated as the sulphate. In the other cases, the ethereal solution is oxidised by lead peroxide and glacial acetic acid, the di-imine is then reduced by zinc dust, and the colourless solution is shaken with sodium carbonate to remove acetic acid. The dry ethereal solution is finally mixed with alcoholic oxalic acid to precipitate the oxalate of the aminodiarylamine.

*Aminodidurylamine*,  $\text{C}_{20}\text{H}_{15}\text{N}_2$ , crystallises in concentric groups of needles, m. p.  $157^\circ$ , and may be oxidised by lead peroxide to *duroquinoneduryldi-imine*,  $\text{C}_6\text{HMe}_3\text{:N:CMe}_3\text{:NH}$ , druses of reddish-brown needles, m. p.  $155\text{--}156^\circ$ , which yields aminodurene and *p*-duroquinone, m. p.  $110^\circ$ , when mixed with an excess of hydrochloric acid.

1-Amino-2:3:5-cumene gives rise to *azocumene* [2:3:5:2':3':5'-hexamethylazobenzene], m. p.  $152\text{--}153^\circ$ , *aminodiecumylamine*,  $\text{C}_{18}\text{H}_{24}\text{N}_2$ , m. p.  $138\text{--}139^\circ$ , and *cumoquinonecumyldi-imine*,  $\text{C}_6\text{H}_3\text{Me}_3\text{:N:C}_6\text{HMe}_3\text{:NH}$ , stout prisms, m. p.  $103^\circ$ .

From *m*-4-xylylidine are prepared *azoxylyene* (2:3:2':3'-tetramethylazobenzene), m. p.  $111^\circ$ , *aminodixylylamine* [4-amino-



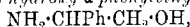
2:3:2':3'-tetramethyldiphenylamine], m. p. 74—75°, and *xyloquinonexylyldi-imine*, brown rosettes, m. p. 67.5—68.5°.

The oxidation of a mixture of aminodurene and *m*-4-xyldine is described. The isolation of the products presents some difficulties, but *xytylaminodurylamine* [4-amino-2:3:5:6:2':3'-hexamethyldiphenylamine], m. p. 153—154°, is certainly identified by its oxidation to *duroquinonexylyldi-imine*, m. p. 83—84°, and hydrolysis of this to duroquinone and the xyldine. *Azodurene* is also present; it forms reddish-yellow tablets, m. p. 80—81°. J. C. W.

**Intramolecular Rearrangement of the Alkylarylamines; Formation of 4-Amino-*n*-butylbenzene.** JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM (T., 1920, 117, 103—137).

**New Method for the Preparation of Alkylamines.** JIRO TAKEDA and SAJURO KURODA (*J. Pharm. Japan*, 1919, 449, 561—608).—Styrene dibromide and carbamide react at 120—130°

to form 2-amino-4-phenyl-4:5-dihydro-oxazole,  $\text{O} \begin{array}{c} \text{CH}_2 - \text{CHPh} \\ \diagup \quad \diagdown \\ \text{C}(\text{NH}_2) \cdot \text{N} \end{array}$ , the hydrolysis of which by alcoholic potassium hydroxide at 150° yields ammonia and  $\beta$ -hydroxy- $\alpha$ -phenylethylamine,



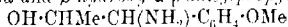
the *dibenzoyl* derivative, m. p. 155°, of which has also been prepared by the following series of reactions, which prove its constitution:  $\text{COPh} \cdot \text{CH}_2 \cdot \text{Br} \rightarrow \text{COPh} \cdot \text{CH}_2 \cdot \text{OAc} \rightarrow \text{COPh} \cdot \text{CH}_2 \cdot \text{OH} \rightarrow \text{NOH} \cdot \text{CPh} \cdot \text{CH}_2 \cdot \text{OH} \rightarrow \text{NH}_3 \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{OH} \rightarrow$ .



On the assumption that the reactions proceed analogously to the preceding, anethole dibromide heated with half its weight of carbamide at 120—130° yields 2-amino-4-*p*-anisyl-5-methyl-4:5-dihydro-

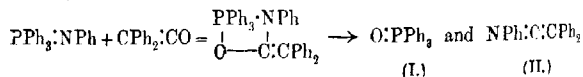
oxazole,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{array}{c} \text{N} = \text{C} \cdot \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{CHMe} \cdot \text{O} \end{array}$ , rectangular columns, m. p.

165°, the hydrolysis of which by alcoholic potassium hydroxide produces ammonia and  $\beta$ -hydroxy- $\alpha$ -*p*-anisylpropylamine,

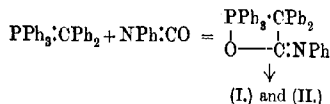


(hydrochloride, m. p. 193°; copper derivative, m. p. 113°). Bromoanethole dibromide and isosafrole dibromide also react with carbamide, yielding corresponding oxazolines, m. p. 20° and 175° respectively. CHEMICAL ABSTRACTS.

**Ketens. XXX. Preparation of a Keten-imine Derivative from Diphenylketen.** H. STAUDINGER and JULES MEYER (*Ber.*, 1920, 53, [B], 72—76).—Triphenylphosphinephenylimine (this vol., i, 107) reacts with diphenylketen in benzene solution in an atmosphere of nitrogen to form triphenylphosphine oxide (I) and diphenylketenphenylimine (II), thus:



The same products are formed when triphenylphosphinediphenylmethyle (ibid., 106) is treated with phenylcarbimide, thus:



In either case, the oxide is precipitated by the addition of light petroleum.

*Diphenylketenphenylimine* crystallises in transparent, pale yellow tablets, m. p. 55–56°, b. p. 190–195°/abs. vac. It has been sought for some time, in order to compare its properties with those of compounds with other systems of twin double linkings, such as ketens,  $-\text{C}:\text{C}:\text{O}$ , and carbimides,  $-\text{N}:\text{C}:\text{O}$ . Quite unexpectedly, the new compound, with the system  $-\text{N}:\text{C}:\text{C}-$ , is very stable and resistant to air, water, alcohol, and bases. When warmed with concentrated hydrochloric acid, however, it yields diphenylacetanilide.

J. C. W.

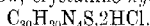
#### Certain Completely Substituted Aromatic Iminosulphides.

H. RIVIER and CH. SCHNEIDER (*Helv. Chim. Acta*, 1920, **3**, 115–134).—The authors give an extended review of the literature relating to the formation of substances containing the group  $\text{C}-\text{S}-\text{C}=\text{N}$ , and their isomerides with the group  $\text{C}-\text{N}-\text{C}=\text{S}$ . The possibility of assigning definite formulæ to the substances is based on the fact that the chromophore,  $\text{C}=\text{S}$ , is much more active than the group,  $\text{C}-\text{S}-\text{C}$ . From this point of view, the authors have revised and extended the work of Jamieson (*A.*, 1904, i, 396), and have prepared a series of compounds which are either yellow or red, and which are therefore held to contain the groups  $-\text{C}-\text{S}-\text{C}-$  and  $\text{C}=\text{S}$  respectively. In only one case has the direct conversion of one form into the other proved possible, but a general consideration of the constitution of the products which have been isolated appears to justify the conclusion that stability is conditioned by symmetry of the molecule. It is, however, remarkable that in the sole instance of actual transformability, conversion is from the symmetrical to the less symmetrical form.

Benzanilide sulphide,  $\text{NPh}:\text{CPh}:\text{S}:\text{CPh}:\text{NPh}$ , intensely yellow prisms, m. p. 211–212° (Jamieson, *loc. cit.*; Raffo and Rossi, *A.*, 1915, i, 86, give 202–204°), is most conveniently prepared by the action of benzanilideiminochloride on the potassium salt of thio-benzanilide. It is converted by hydrogen chloride in ethereal solution into the corresponding *chloride*, an amorphous, red mass, which is decomposed on exposure to moist air.

$\alpha$ -Thiobenzonaphthalide, yellow crystals, m. p. 149–150°, and  $\beta$ -thiobenzonaphthalide, yellow leaflets, m. p. 160–162°, are prepared by the action of phosphorus pentasulphide on a solution of the corresponding benzonaphthalides in solvent naphtha.  $\alpha$ -Benzonaphthalide sulphide,  $\text{S}(\text{CPh}:\text{N}:\text{C}_{10}\text{H}_7)_2$ , yellow, crystalline powder, m. p. 130–131°, is formed in the same manner as benzanilide

sulphide; when its solutions are boiled for some time or are evaporated, it becomes transformed into *thiobenzoyl-di- $\alpha$ -naphthylbenzenylamidine*,  $C_{10}H_7 \cdot N \cdot CPh \cdot N(C_{10}H_7) \cdot CPh \cdot S$ , red crystals, m. p. 156—157°, but the reverse change could not be effected. Hydrogen chloride and concentrated sulphuric acid convert the yellow substance into red salts, which are decomposed by excess of acid, whilst the red material is decomposed by acid, with formation of benznaphthalide and thiobenznaphthalide. The action of benzanilide iminochloride on potassium  $\alpha$ -thiobenznaphthalide or of  $\alpha$ -benznaphthalide iminochloride on potassium thiobenzanilide yields the substance,  $NPh \cdot CPh \cdot S \cdot CPh \cdot N \cdot C_{10}H_7$ , yellow crystals, m. p. 176—177°, which yields an unstable, red *hydrochloride*, which is decomposed by excess of acid into thiobenzanilide and  $\alpha$ -benznaphthalide, showing that in the transformation which precedes the decomposition, it is the group  $NPh$ , and not  $N \cdot C_{10}H_7$ , which has exchanged places with the sulphur atom. Attempts to prepare  $\beta$ -benznaphthalide sulphide or the sulphide of benzanilide and  $\beta$ -benznaphthalide were unsuccessful. *p*-Dimethylaminobenzanilide sulphide,  $S[C(C_6H_4 \cdot NMe_2) \cdot NPh]_2$ , yellow needles or prisms, m. p. 155—156°, is best prepared by the action of potassium sulphide on *p*-dimethylaminobenzanilideiminochloride hydrochloride; it yields a yellow, crystalline *hydrochloride*,



Excess of hydrochloric or sulphuric acid does not decompose the salts, which thus appear to have the same constitution as the free base.

The action of thiobenzoyl chloride,  $Ph \cdot CSCOCl$ , on diphenylbenzenylamidine, on *di- $\alpha$ -naphthylbenzenylamidine*, pale yellow leaflets, m. p. 160—161°, and on *di- $\beta$ -naphthylbenzenylamidine*, colourless crystals, m. p. 154—155°, has been investigated; in the first case, benzanilide sulphide was obtained, whilst positive results were not given by the naphthalene derivatives.

Benzoylthiobenzanilide,  $COPh \cdot NPh \cdot CSPh$ , red prisms, m. p. 108—109° (compare Jamieson, *loc. cit.*), *benzoyl- $\alpha$ -thiobenznaphthalide*, red crystals, m. p. 145—146°, and *benzoyl- $\beta$ -thiobenznaphthalide*, red crystals, m. p. 129—130°, were prepared by the gradual addition of a solution of benzoyl chloride in chloroform to the requisite thioanilide or thiobenznaphthalide dissolved in the calculated quantity of alcoholic potassium hydroxide. They are decomposed by hydrogen chloride in ethereal solution, even if only one molecular proportion of the acid is used, yielding benzoyl chloride and the corresponding thioanilide. They are soluble in concentrated sulphuric acid without decomposition, but addition of water precipitates the thioanilide. II. W.

**[Preparation of] Phenolic Compounds.** E. H. ZOLLINGER and H. ROERLING (U.S. Pat. 1321271).—Lead compounds which form insoluble or sparingly soluble compounds with phenols are made to react with aromatic halogen compounds and a hydroxide of an alkali or alkaline earth metal. The reaction is facilitated by

catalysts, such as copper or copper compounds, iodides of alkali or alkaline earth metals, iodates, vanadium, titanium, molybdenum, and rare earths and their salts. Thus *o*-chlorophenol is heated for about forty-five minutes at 250° with an aqueous solution of lead acetate and sodium hydroxide (alternatively, lead sulphate or hydroxide at 260° with copper iodide as catalyst), whereby the lead salt of catechol is formed, which crystallises on cooling.

Among the examples recorded is the formation of cresolsulphonic acid from chloro- or bromo-toluenesulphonic acids, orcinol from bromocresol or dibromotoluene, catechol-4-sulphonic acid from sodium 1:2-dichlorobenzene-4-sulphonate, 3:5-dihydroxybenzoic acid from 3:5-dihalogenobenzoic acids, salicylaldehyde from *o*-chlorobenzaldehyde,  $\alpha$ - and  $\beta$ -naphthols from the respective chloronaphthalenes, and alizarin from 1:2-dichloroanthraquinone.

CHEMICAL ABSTRACTS.

**The Preparation of 2:4-Dinitrophenetole and 2:4:6-Trinitrophenetole.** M. MARQUEYROL and SCOHY (*Bull. Soc. chim.*, 1920, [iv], 27, 105—107).—2:4-Dinitrophenetole may readily be prepared by the action of aqueous sodium hydroxide on an alcoholic solution of 1-chloro-2:4-dinitrobenzene at 36°, gradually rising to 55°. If this phenetole is then nitrated in sulphuric acid solution at 30—40°, an excellent yield of 2:4:6-trinitrophenetole is obtained. W. G.

**The Synthesis of Aldehydes and Hydroxy-acids by means of Secondary *aaa*-Trichloro-alcohols.** PIERRE HÉBERT (*Bull. Soc. chim.*, 1920, [iv], 27, 45—55).—Bossneck's method for the preparation of aldehydes or hydroxy-acids by the action of potassium hydroxide on *aaa*-trichloro-secondary alcohols (compare A., 1885, 976; 1886, 458) is shown to be generally applicable in the aliphatic, cyclic, aromatic, naphthalene, and aryl aliphatic series. The potassium hydroxide may be replaced by the hydroxides of sodium, calcium, magnesium, or barium, or advantageously by sodium carbonate. The trichloro-alcohols of the aliphatic series do not give such good yields as do the aromatic alcohols, where the  $\cdot\text{CH}(\text{OH})\cdot$  group is directly attached to a ring carbon atom. The activity in the aromatic series is diminished if this group is separated from the nucleus by one or more carbon atoms. The following new compounds are described.

By condensing magnesium *p*-bromophenyl bromide with anhydrous chloral,  $\beta$ -*p*-bromophenyltrichloromethylcarbinol,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$ ,

b. p. 183—187°/18 mm., is obtained, giving an *acetate*, m. p. 145—147°, and this on decomposition with sodium carbonate gives *p*-bromobenzaldehyde and *p*-bromophenylglycollic acid.

Magnesium benzyl bromide reacts with chloral to give *phenyl-trichloroisopropyl alcohol*,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$ , b. p. 158—160°/18 mm., giving an *acetate*, m. p. 110—111°.

*o*-4-Xylyltrichloromethylcarbinol is decomposed by sodium

carbonate, giving 3:4-dimethylbenzaldehyde and 3:4-dimethyl-phenylglycollic acid,  $C_6H_3Me_2 \cdot CH(OH) \cdot CO_2H$ , m. p. 115–116°.

Ethyl  $\alpha$ -naphthylglycollate,  $C_{10}H_7 \cdot CH(OH) \cdot CO_2Et$ , has m. p. 68–69°. W. G.

**Mercury Benzoate.** ROBERT WOOD TERRY (*Medl. Drug. and Pharm. Rev.*, 1919, **53**, 222–225; from *Chem. Zentr.*, 1919, iii, 866).—A 1% solution of mercury benzoate is obtained by dissolving 2.715 parts of mercuric chloride and 2.880 parts of sodium benzoate in 442 parts of water, and filtering after a week.

H. W.

**Abietic Acid.** DAVID JOHANSSON (*Arkiv Kem. Min. Geol.*, 1917, **6**, No. 19).—Very little is known as to the derivatives and decomposition products of abietic acid. The author has therefore sought evidence of its unsaturation and of the presence in its molecule of the aromatic and hydroaromatic nuclei postulated by previous investigators (compare Easterfield and Bagley, T., 1904, 1238; Levy, A., 1913, i, 620). The acid, prepared from American colophony by Hunt and Pochin's process, had m. p. 168–173° (sintering at 155°), and in alcoholic solution  $[\alpha]_D^{20} -28.6^\circ$ . Both the Hübl-Waller and the Winkler iodine numbers increased with the duration of the determination, respective values of 102–171 and 150–357 being obtained. Since, approximately, the same values were obtained from the dihydro-derivative (below), and this behaviour was reproduced by the congener *d*-pimaric acid and its dihydro-derivative, it would appear that the unreduced acids contain at least two double bonds, which are not equivalent, or that substitution takes place. Halogenated compounds could not, however, be isolated. Dihydroabietic acid,  $C_{20}H_{32}O_2$ , m. p. 173–178° (sintering at 156°), was obtained by hydrogenation in ethereal solution in presence of platinum-black. Unlike abietic acid, it is unchanged after long exposure. Treated with chloroform and glacial acetic and sulphuric acids, it gives a reddish-violet colour, changing to yellowish-brown, whilst abietic acid gives a deep blue colour, which becomes brownish-green. From sulphonation experiments, a very small proportion of a mixture of acids was obtained. Dinitroabietic acid,  $C_{20}H_{28}O_2(NO_2)_2$ , produced by nitration with fuming acid below 10°, separates from acetone in needles, m. p. 178–184°,  $[\alpha]_D^{20} +44.26^\circ$ , which, on exposure to sunlight, turn red in a few seconds, and eventually brownish-green. The sodium salt,  $C_{20}H_{27}O_2(NO_2)_2 \cdot Na, 11H_2O$ , needles, the potassium salt, and the barium salt,  $[C_{20}H_{25}O_2(NO_2)_2]_2Ba \cdot 4H_2O$ , yellowish-white needles, crystallise much better than those of abietic acid; the silver salt,  $C_{20}H_{25}O_2(NO_2)_2 \cdot Ag$ , is a flocculent precipitate. In contrast with abietic acid, its dinitro-derivative is esterified by treatment with alcohol and hydrochloric acid. The methyl ester forms needles, m. p. 178–182°. The ethyl ester,

$C_{20}H_{27}(NO_2)_2 \cdot CO_2Et$ , needles, m. p. 156–158°, is best prepared from the silver salt, and

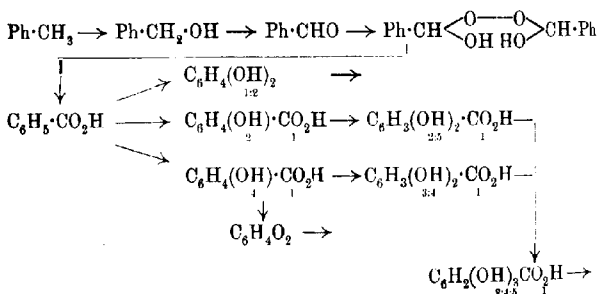
is only hydrolysed by alkali with difficulty. Molecular compounds of the dinitro-derivative with, in some cases, four, and in others six, molecular proportions of naphthalene, anthracene, phenanthrene, and retene separate from alcohol in white needles, stable to light, which respectively melt at 110–117° (decomp.), 244–246°, 235–236°, and 234–238°. *Diamino-abietic acid dihydrochloride*,  $C_{20}H_{28}O_2(NH_2.HCl)_2$ , is a brown, amorphous powder, m. p. 280°, and very hygroscopic. A tarry product was obtained in an attempt to remove the amino-group by diazotisation. Crystallographic data are given for abietic, dihydroabietic, and dihydrodextropimaric acids. The presence of an aromatic or hydroaromatic nucleus in the molecule of abietic acid is regarded as now definitely determined. J. K.

**The Action of Nitrites on some Imino-ethers.** A. BERTON (*Arkiv Kem. Min. Geol.*, 1918–1919, 7, No. 13, 1–21).—The product of the action of nitrous acid on ethyl benzoyliminoacetate is not a nitroso-derivative (Haller, A., 1887, 826), but is identical with ethyl oximinobenzoylacetate (Perkin, T., 1885, 47, 243). *Ethyl imino-oximinobenzoylacetate*,  $COPh \cdot C(NO_2) \cdot C(NH) \cdot OEt$ , leaflets, m. p. 112°, is obtained as the intermediate product when a cold solution of ethyl iminobenzoylacetate is added to a cold solution of sodium nitrite, and passes into ethyl oximinobenzoylacetate on warming or when treated with acids. Further, chloro-oximinoacetophenone, by treatment with potassium cyanide and hydrochloric acid, furnishes oximinobenzoylacetoneitrile (E. v. Meyer, A., 1885, 582), which is converted by hydrochloric acid in alcoholic solution into the hydrochloride of ethyl imino-oximinobenzoylacetate. The *hydrochloride*,  $C_{11}H_{13}O_2N_2Cl$ , m. p. 114°, is precipitated by leading dry hydrogen chloride into its ethereal solution. It can also be similarly obtained from the product of the action of amyl nitrite on an ethereal solution of ethyl iminobenzoylacetate, whilst, by passing dry ammonia into a similar solution or a solution of ethyl imino-oximinobenzoylacetate in alcohol, *oximino-benzoylacetamidine*,  $C_9H_9O_2N_3$ , sulphur-yellow crystals, m. p. 227–229°, is produced. Its *hydrochloride*,  $C_9H_{10}O_2N_3Cl$ , is faintly yellow, and begins to lose hydrochloric acid at 200°. The *sulphate*,  $C_9H_{11}O_2N_3S$ , melts at 195°.

The action of nitrous acid on ethyl iminophenylacetate leads to the formation of ethyl phenylacetate and phenylacetamidine nitrite,  $CH_2Ph \cdot C(NH) \cdot NH_2 \cdot HNO_2$  (Lossen, *Diss.*, Koenigsberg, 1890; Kammer, *ibid.*, 1893), m. p. 147°. This compound was further identified by the preparation of its acetate, m. p. 195°, and its nitrate, m. p. 166–167°, and its conversion into phenylacetamide by the action of sodium hydroxide.

In agreement with Knorr's view (A., 1917, i, 255) that the formation of amidines by the action of ammonia on the hydrochlorides of imino-esters is conditioned by ammonium chloride, it is shown that the nitrate of *p*-tolylacetamidine is produced by the action of ammonium nitrate on ethyl imino-*p*-tolylacetate. J. K.

Measurements of potential with toluene, benzyl alcohol, benzaldehyde, and benzoic acid, respectively, show a rapid and remarkable increase of anodic polarisation in the case of the aldehyde; the same phenomenon is observed to a much smaller degree with benzyl alcohol and toluene, whilst with benzoic acid, anodic polarisation is very feeble; the results show that it is impossible so to control electrolytic oxidation that only benzyl alcohol is produced, and also that benzoic acid can be further oxidised even in the presence of an excess of toluene. The peculiar behaviour of benzaldehyde is attributed to the formation of a peroxide, presumably either dibenzylidene peroxide hydrate or dibenzylidene peroxide, since evidence of the production of the volatile benzoic peracid,  $\text{Ph}\cdot\text{CO}_3\text{H}$ .



could not be obtained. The electrolytic oxidation of toluene thus follows the lines of the scheme on the previous page. H. W.

**A New Method of Synthesis of Indenic Ketones.** A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], 25, 597—598).—An application of the method previously described for the synthesis of indene derivatives (compare A., 1914, i, 265). When benzylidene-deoxybenzoin dibromide is heated at 140—145°, it loses two molecules of hydrogen bromide and gives diphenylindone, m. p. 151—152°; this yields a *phenylhydrazone*, m. p. 175—176°.

W. G.

**Action of Cyanogen and its Haloids on Mixed Organo-magnesium Derivatives. New Methods of Synthesis of Nitriles and Ketones. New Method of Introduction of a Halogen into an Organic Molecule.** V. GRIGNARD, E. BELLET, and CH. COURTOT (*Ann. Chim.*, 1919, [ix], 12, 364—393. Compare A., 1916, i, 487).—The first part of the paper is a more detailed account of work already published (compare A., 1911, i, 292; 1912, i, 623; 1914, i, 391). By using 2 mols. of the magnesium alkyl or aryl haloid to 1 mol. of cyanogen chloride, a ketimine results which, when hydrolysed with water or dilute hydrochloric acid, gives the corresponding ketone (A., 1914, i, 391). In this way, the authors have prepared benzophenone, 4:4'-dimethylbenzophenone, 2:2'-dimethylbenzophenone, m. p. 72°, giving an *oxime*, m. p. 105°,  $\alpha\alpha$ -dinaphthyl ketone, 2:4-dimethylbenzophenone, and phenyl  $\alpha$ -naphthyl ketone.

W. G.

**Derivatives of Naphthyl- $\beta$ -ethylamine.** ANTONIO MADINA-VEITIA (*Bull. Soc. chim.*, 1919, [iv], 25, 601—610; *Anal. Fis. Quim.*, 1918, 16, 543—545).—The author has prepared a number of naphthalene derivatives having a side-chain with an amino-group in the  $\beta$ -position with the view of studying their action on the sympathetic nervous system in comparison with that of  $\beta$ -methylamino- $\alpha$ -phenylethane and its derivatives.

$\alpha$ -Chloro- $\beta$ -bromo- $\alpha$ -methoxyethane when added to a solution of magnesium in bromobenzene and ether gives  $\beta$ -bromo- $\alpha$ -methoxy- $\alpha$ -phenylethane, b. p. 125—127°/15 mm., which when heated with methylamine in benzene solution at 100° for three hours gives  $\beta$ -methylamino- $\alpha$ -methoxy- $\alpha$ -phenylethane, b. p. 105—106°/22 mm., giving a *hydrochloride* and a *platinichloride*, m. p. 189° (decomp.).  $\beta$ -Methylamino- $\alpha$ -methoxy- $\alpha$ -naphthylethane is similarly prepared, with the intermediate formation of  $\beta$ -bromo- $\alpha$ -methoxy- $\alpha$ -naphthylethane, b. p. 185—190°/14 mm., and gives a *hydrochloride* and a *platinichloride*.

$\alpha$ -Naphthyl methyl ketone, when acted on by amyl nitrite in the presence of sodium ethoxide, gives  $\alpha$ -naphthyl nitrosomethyl ketone, giving a *sodium salt*, and this nitroso-derivative, when reduced with stannous chloride and hydrochloric acid, yields  $\alpha$ -naphthyl aminomethyl ketone,  $C_{10}H_7\cdot CO\cdot CH_2\cdot NH_2$ , giving a *hydrochloride*.



Similarly, 4-methoxy- $\alpha$ -naphthyl methyl ketone gives a *nitroso-derivative*, which on reduction yields 4-methoxy- $\alpha$ -naphthyl amino-methyl ketone, isolated as its *hydrochloride*, which when heated in a sealed tube for four hours at 100° with fuming hydrochloric acid gives 4-hydroxy- $\alpha$ -naphthyl aminomethyl ketone, isolated as its *hydrochloride*.

The vaso-constrictive action of these substances has been studied by Trendelenburg's method. It is shown that the introduction of a methoxy-group into the side-chain has little or no influence on the physiological action of the substance, but the replacement of the phenyl nucleus by a naphthyl nucleus has a very marked effect, increasing the vaso-constrictive action about forty times in the case of the substances studied. 4-Hydroxy- $\alpha$ -naphthyl aminomethyl ketone possesses a very marked vaso-constrictive action, which is much greater than that of the corresponding derivative without the hydroxyl group or than that of the corresponding derivative without the carbonyl group in the side-chain.

W. G.

**The Constitution of Dypnopinacone and its Derivatives.**  
**IV. The Luteo-dypnopinacones.** MAURICE DELACRE (*Ann. Chim.*, 1919, [ix], 12, 394—425. Compare A., 1914, i, 1068; 1916, i, 479; 1918, i, 539; this vol., i, 165).—A more detailed account of work already published (compare A., 1891, 456; 1896, i, 662).

W. G.

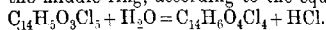
**[Preparation of] *p*-Benzoquinone from Benzene.** J. M. WEISS and C. R. DOWNS (U.S. Pat. 1318631).—A mixture of benzene and oxygen or air in the form of vapour or spray is passed over pumice impregnated with vanadium oxide and heated at 300—700°. *p*-Benzoquinone, maleic acid, and by-products are obtained, together with unchanged benzene. As substitutes for the catalyst, vanadium or vanadium compounds, molybdenum, tungsten, gold, ruthenium, cobalt, or the oxides of copper, manganese, cobalt, lead, chromium, antimony, cadmium, and thorium, may be used. The reaction may be carried out at pressures greater than, equal to, or less than atmospheric pressure. After removal of maleic acid by crystallisation or by solution in water, the remaining liquid products may be again passed over the catalyst to effect further oxidation, with the production of additional *p*-benzoquinone and maleic acid.

CHEMICAL ABSTRACTS.

**A Novel Degradation in the Anthraquinone Series.** K. FRIES and E. AUFFENBERG (*Ber.*, 1920, 53, [B], 23—28).—When the hydrochloride of 1-aminoanthraquinone is exhaustively chlorinated in glacial acetic acid, it yields 2:2:3:4:4-pentachloro-1-keto-1:2:3:4-tetrahydroanthraquinone,  $C_6H_4$   $\begin{matrix} \text{CO} \cdot \text{C} \cdot \text{CO} \cdot \text{CCl}_2 \\ \text{CO} \cdot \text{C} \cdot \text{CCl}_2 \cdot \text{CHCl} \end{matrix}$ , which crystallises in rhombic tablets, m. p. 166—168° (slight decomp.), and may be reduced by stannous chloride to 2:4-dichloro-1-hydroxyanthraquinone, slender, orange-coloured needles, m. p.

242°. The compound may also be reduced by boiling an acetic acid solution with ammonium chloride, the product being 2:3:4-trichloro-1-hydroxyanthraquinone, which crystallises in orange needles, m. p. 214°, forms sparingly soluble, brilliant red alkali salts, and is remarkably stable towards chlorine or concentrated nitric and sulphuric acids.

The pentachloro-derivative undergoes a novel hydrolysis when warmed with concentrated sulphuric acid, the product being o-2:3:4:6-tetrachloro-5-hydroxybenzoylbenzoic acid, formed by the rupture of the middle ring, according to the equation

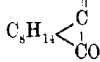


It crystallises in minute druses, m. p. 277—278°, forms a sparingly soluble sodium salt and an acetate, m. p. 213°, and is hydrolysed by heating at a higher temperature with sulphuric acid to phthalic acid and 2:3:4:5-tetrachlorophenol. The same derivative of benzoylbenzoic acid is formed as a by-product when the original, crude chlorination product, containing ammonium chloride, is boiled with acetic acid, but it is not given by the main product of this reaction, namely, the above trichlorohydroxyanthraquinone.

J. C. W.

### Stereoisomeric Derivatives of Aminomethylenecamphor.

I. HANS RUPF, MAX SEIBERTH, and WALTER KUSSMAUL (*Helv. Chim. Acta*, 1920, 3, 50—70).—Aminomethylenecamphor and many of its derivatives are found to exist in two forms, characterised by lower melting point and generally greater solubility, and higher melting point and usually more sparing solubility; these are designated  $\beta$ - and  $\alpha$ -compounds respectively. In general, they are readily mutually transformable. Since a new asymmetric carbon atom is not developed during the formation of these substances, optical isomerism is out of the question, and it appears certain that instances of *cis-trans*-isomerism (annexed formula) are being dealt



with, although direct experimental evidence on this point is lacking. The optical investigation of these substances promises results of considerable interest, since but few optically active *cis-trans*-isomerides have been examined; the sparing solubility of the products at the ordinary temperature and the ease with which they undergo transformation when the temperature is raised have prevented an extended examination, and the results which have been obtained so far do not allow any general conclusions to be drawn.

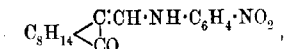
A considerable improvement in the preparation of hydroxymethylenecamphor is effected if the sodium camphor is prepared by the interaction of camphor and sodamide in benzene solution; under these conditions, the formation of borneol is avoided, and any unattacked camphor can be recovered.

$\alpha$ -Aminomethylenecamphor is conveniently prepared by heating

hydroxymethylenecamphor with saturated aqueous ammonia under pressure at  $100^{\circ}$ ; it forms colourless, shining leaflets, m. p.  $156^{\circ}$ ,  $D_4^{20}$  0.8176,  $[\alpha]_D^{20} + 191.37^{\circ}$ ,  $[\alpha]_B^{20} + 257.32^{\circ}$ ,  $[\alpha]_{Hg}^{20} + 323.41^{\circ}$ ,  $[\alpha]_D^{20} + 477.19^{\circ}$ ,  $[\alpha]_F/[\alpha]_C$  2.48 in alcoholic solution. When distilled under diminished pressure, it is quantitatively converted into the  $\beta$ -form, m. p.  $103-104^{\circ}$ ,  $D_4^{20}$  0.8159,  $[\alpha]_D^{20} + 236.57^{\circ}$ ,  $[\alpha]_B^{20} + 313.76^{\circ}$ ,  $[\alpha]_F^{20} + 388.23^{\circ}$ ,  $[\alpha]_F^{20}$  553.99°,  $[\alpha]_F/[\alpha]_C$  2.34. The latter is very labile, but can be preserved unchanged in substance, even if exposed to sunlight; it is converted into the  $\alpha$ -form if its solution in alcohol or benzene is evaporated, when the benzene solution is exposed to sunlight, or when the alcoholic solution is boiled.

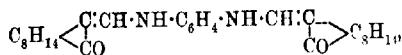
$\alpha$ -Benzoylaminoethylenecamphor is the sole product of the action of benzamide on hydroxymethylenecamphor in glacial acetic acid solution, and is formed, together with the  $\beta$ -isomeride, by the benzylation of aminomethylenecamphor in pyridine solution; it forms slender, colourless needles, m. p.  $208^{\circ}$ ,  $D_4^{20}$  0.9838,  $[\alpha]_D^{20} + 164.28^{\circ}$ ,  $[\alpha]_B^{20} + 219.29^{\circ}$ ,  $[\alpha]_{Hg}^{20} + 273.15^{\circ}$ ,  $[\alpha] + 393.06^{\circ}$ ,  $[\alpha]_F/[\alpha]_C$  2.39 in pyridine solution. The  $\beta$ -modification crystallises in monoclinic prisms  $[a:b:c=0.96402:1:1.05011, \beta=110^{\circ}40']$ , m. p.  $112^{\circ}$ ,  $D_4^{20}$  0.9833,  $[\alpha]_D^{20} + 166.44^{\circ}$ ,  $[\alpha]_B^{20} + 228.29^{\circ}$ ,  $[\alpha]_{Hg}^{20} + 292.67^{\circ}$ ,  $[\alpha]_F^{20} + 453.11^{\circ}$ ,  $[\alpha]_F/[\alpha]_C$  2.72; it is converted into the  $\alpha$ -variety when its solution in light petroleum is exposed to ultra-violet light, but not by treatment with hydrogen chloride in alcoholic or light petroleum solution. The reverse transformation is effected by boiling a solution of the  $\alpha$ -form in pyridine.

$\alpha$ - and  $\beta$ -*p*-Nitroanilinomethylenecamphor,

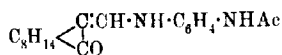


are simultaneously formed by the action of *p*-nitroaniline on hydroxymethylenecamphor in glacial acetic acid solution, and are separated by taking advantage of the greater solubility of the  $\beta$ -isomeride in cold benzene. The  $\alpha$ -form crystallises in canary-yellow leaflets, m. p.  $180-181^{\circ}$ , and slowly passes into the  $\beta$ -isomeride at the ordinary temperature, rapidly at  $200^{\circ}$ ; the  $\beta$ -isomeride forms orange-yellow needles with a violet reflex, m. p.  $151-152^{\circ}$ , and is converted into the  $\alpha$ -form when its solution in boiling alcohol is exposed to direct sunlight.

*p*-Phenylenediaminodimethylenecamphor,



pale yellowish-green, microscopic needles, m. p.  $276-277^{\circ}$ , appears to be the sole product of the action of *p*-phenylenediamine on hydroxymethylenecamphor; it could only be obtained in one form. *p*-Acetylaminonitroanilinomethylenecamphor,



forms pale yellowish-green leaflets, m. p. 226—227°, and exists in one form only. *p*-Aminoanilinomethylenecamphor could not be obtained by the reduction of the corresponding nitro-compound by iron and acetic acid; although reduction appears to occur, the amino-derivative is immediately hydrolysed, and condensation then occurs between the *p*-phenylenediamine and hydroxymethylenecamphor, which are thus formed with the ultimate production of *p*-phenylenediaminodimethylenecamphor; reduction could not be effected with ammonium sulphide, whilst with sodium sulphide either form of the nitro-compound yields the same amino-derivative in poor yield. The pure amine, m. p. 163°, is, however, obtained by the action of ethyl-alcoholic potassium hydroxide on the corresponding acetyl derivative. The *hydrochloride* is sparingly soluble in water and cannot be diazotised.

*p*-Phenetidinomethylenecamphor ( $\beta$ -form, coarse plates and prisms, m. p. 111—112°;  $\alpha$ -form, pale yellowish-green leaflets, m. p. 166—167°) is prepared by the action of *p*-phenetidine on hydroxymethylenecamphor in alcoholic solution, and is separated into its isomerides by fractional crystallisation from benzene. The  $\beta$ -variety is very labile, and is converted into the  $\alpha$ -variety when attempts are made to recrystallise it from alcohol; it has not been found possible to effect the reverse transformation. H. W.

### Stereoisomeric Derivatives of Aminomethylenecamphor.

II. HANS RUPE, MAX SEIBERTH, and WALTER KUSSMAUL (*Helv. Chim. Acta*, 1920, **3**, 71—89).—A continuation of the work described in the preceding abstract.

*Diethylaminomethylenecamphor*,  $C_{12}H_{19}N$ ,  $\begin{matrix} \text{C} \cdot \text{CH} \cdot \text{NEt}_2 \\ | \\ \text{CO} \end{matrix}$ , is obtained

as a pale yellow, viscous oil, b. p. 175—175.5°/11 mm., which solidifies when cooled to a mass of transparent plates, m. p. 20—22°, by the action of diethylamine on hydroxymethylenecamphor or chloromethylenecamphor. The *hydrochloride* is slowly decomposed in aqueous solution, yielding hydroxymethylenecamphor and diethylamine hydrochloride. *Piperidinomethylenecamphor* is a pale yellow, viscous oil, b. p. 203—204°/11 mm., m. p. 60° after softening at 58°; the *hydrochloride*, slender needles, suffers first dissociation and then hydrolysis in aqueous solution. *Tetrahydroquinolinomethylenecamphor* forms coarse, transparent prisms, m. p.

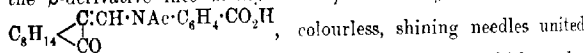
109°. *Carbamidomethylenecamphor*,  $C_8H_{13}N_2O$ ,  $\begin{matrix} \text{C} \cdot \text{CH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2 \\ | \\ \text{CO} \end{matrix}$ ,

prepared by melting the components together or by condensation in glacial acetic acid solution, crystallises in needles, m. p. 197°; a second modification, which does not melt below 280°, possibly exists.  $\beta$ -Ethylurethanomethylenecamphor is exclusively obtained when its components are heated together at 110°, and forms a colourless, odourless, highly refractive oil, which does not solidify in a mixture of ice and salt, and rapidly becomes yellow or red when preserved; it has b. p. 178—179°/10 mm.,  $D_4^{20}$  0.9835,  $[\alpha]_D^{20} + 145.93^\circ$ ,  $[\alpha]_D^{25} + 197.17^\circ$ ,  $[\alpha]_{H\alpha}^{20} + 247.62^\circ$ ,  $[\alpha]_F^{20} + 366.69^\circ$ ,  $[\alpha]_D/[\alpha]_C$

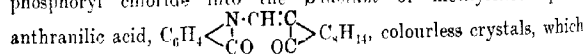
2.51 in pyridine solution. When, however, the components are mixed in glacial acetic acid solution, the  $\alpha$ -variety is mainly formed at the ordinary temperature, but the reaction is very incomplete, whilst at a higher temperature reaction proceeds quantitatively, but yields more of the  $\beta$ -variety. The  $\alpha$ -isomeride forms colourless, many-sided crystals, m. p.  $162^\circ$ ,  $D_4^{20}$  0.98352,  $[\alpha]_D^{20} + 149.42^\circ$ ,  $[\alpha]_D^{20} + 198.52^\circ$ ,  $[\alpha]_{H_2}^{20} + 245.11^\circ$ ,  $[\alpha]_F^{20} + 347.35^\circ$ ,  $[\alpha]_F/[\alpha]_C$  2.32. Transformation of the  $\beta$ - into the  $\alpha$ -variety can be effected by hydrogen bromide, hydrogen chloride, concentrated sulphuric acid, nitrous fumes, iodine in ethereal solution, by exposure to direct sunlight, and by preservation in the dark. The reverse action is effected by boiling a solution of the  $\alpha$ -variety in glacial acetic acid with exclusion of light.

The two forms of *ethyl methylenecamphor-p-aminobenzoate* are simultaneously formed by the condensation of the components in glacial acetic acid solution, and are separated with the aid of light petroleum; the  $\alpha$ -variety crystallises in minute needles, m. p.  $176^\circ$ , whilst the  $\beta$ -form has m. p.  $105^\circ$ . The former modification is exclusively formed when a mixture of the components is gently heated; it appears to be exceptionally stable, but undergoes partial transformation when its solution in formic acid is boiled during a protracted period in direct sunlight and in the presence of iodine.

The *methylenecamphoranthranilic acids* are simultaneously formed from hydroxymethylenecamphor and anthranilic acid in glacial acetic acid solution, and can be separated to some extent mechanically, owing to the difference in their crystalline forms. Separation by means of solvents is impracticable, owing to their very similar solubilities. Isolation of the  $\beta$ -variety is best effected by boiling the mixture of isomerides with benzene, when the  $\alpha$ -variety passes into the  $\beta$ -form, almost colourless needles, which rapidly become brown, and have m. p.  $112^\circ$  and  $176^\circ$  after re-solidifying. The  $\alpha$ -variety is conveniently obtained by boiling a solution of the  $\beta$ -form in toluene, and forms pale brown, many-sided crystals, m. p.  $176^\circ$ ; the latter isomeride is exclusively formed when the components are heated together, the result being attributable to the high temperature of the reaction. Attempts to convert the methylenecamphoranthranilic acids into indole or indigo-derivatives were unsuccessful. Acetic anhydride, however, converts the  $\beta$ -derivative into *methylenecamphor-N-acetyl-anthranilic acid*,

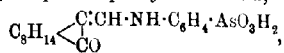


in clusters, m. p.  $185^\circ$ , to an intensely green liquid, which gradually becomes reddish-brown. Either variety is transformed by phosphoryl chloride into the  $\beta$ -lactam of methylenecamphor-



immediately become discoloured on exposure to air and have m. p.  $165^\circ$ . The substance is converted by boiling water into methylenecamphoranthranilic acid, and by cold alkali into a mixture of the sodium salts of the two forms of the acid.

*Methylenecamphor-p-aminophenylarsinic acid,*



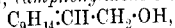
is best obtained as *sodium* salt by heating hydroxymethylenecamphor with atoxyl at  $110^\circ$ ; it forms slender, colourless needles, which decompose at  $220^\circ$  and melt indistinctly at  $250^\circ$ ; anilino-methylenecamphor, m. p.  $168-170^\circ$ , and a substance,  $\text{C}_{27}\text{H}_{40}\text{O}_2$ , slender, yellow needles, m. p.  $188^\circ$ , are formed as by-products during the condensation.

H. W.

**Transpositions in the Camphene Series.** G. LANGLOIS (*Ann. Chim.*, 1919, [ix], 12, 265—363. Compare this vol., i, 171). — By the direct bromination of camphene in anhydrous ether,  $\omega$ -bromocamphene, b. p.  $115-120^\circ/15$  mm.,  $225-226^\circ/760$  mm.,  $D^{15}_4$  1.265,  $[\alpha]_D + 68.85^\circ$ , is obtained, its constitution being proved by its behaviour on oxidation either by nitrous vapour or by potassium permanganate, camphenylone being the product in either case. In the preparation of a magnesium derivative from bromocamphene, some *dehydrodicamphene*,  $\text{C}_{10}\text{H}_{13}\cdot\text{C}_{10}\text{H}_{15}$ , m. p.  $181^\circ$ , is obtained. The magnesium derivative when acted on by carbon dioxide gives an *acid*,  $\text{C}_{10}\text{H}_{15}\cdot\text{CO}_2\text{H}$ , m. p.  $124-125^\circ$ , which on oxidation also gives camphenylone and oxalic acid.  $\omega$ -Bromocamphene is stable towards Beckmann's oxidising mixture, and with hydrogen bromide yields 2- $\omega$ -dibromocamphane, the latter change being reversible. Attempts to replace the bromine in bromocamphene with a phenyl group by means of magnesium phenyl bromide were not very successful, whilst with magnesium methyl iodide the product was *cymene*. On chlorination in ether, bromocamphene gives *dichlorobromocamphene*,  $\text{C}_{10}\text{H}_{13}\text{Cl}_2\text{Br}$ , m. p.  $74^\circ$ . Hydrogen chloride in the cold is without action on bromocamphene, but when passed into an acetic acid solution at  $100^\circ$  it yields dibromocamphane. As compared with camphene, bromocamphene only undergoes very slow acetylation, and the product is not characterised.

By carefully restricted chlorination of camphene, a certain amount of chlorocamphene, b. p.  $95-98^\circ/15$  mm.,  $D^{15}_4$  1.016—1.017,  $[\alpha]_D + 37^\circ$ , is obtained, which is not acted on by any hydrogen chloride or by Beckmann's oxidising agent. With potassium permanganate, it is oxidised to camphenylone. With hydrogen bromide, it gives  $\omega$ -chloro-2-bromocamphane, m. p.  $103^\circ$ , and on further chlorination it gives trichlorocamphene, m. p.  $104^\circ$ . On bromination it gives *chlorodibromocamphene*,  $\text{C}_{10}\text{H}_{13}\text{ClBr}_2$ , m. p.  $64-65^\circ$ .

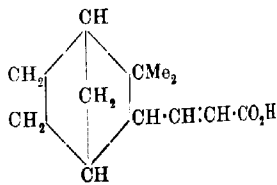
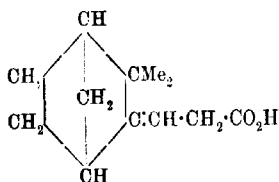
When camphene is heated on an oil-bath for two days with a mixture of trioxymethylene and acetic acid, it gives an *acetate*,  $\text{C}_{11}\text{H}_{17}\cdot\text{CO}_2\text{CH}_3$ , b. p.  $130-135^\circ/20$  mm., which on hydrolysis gives a primary alcohol, *camphenylidene-6-ethanol*,



b. p.  $125-126^\circ/8$  mm.,  $135^\circ/17$  mm.,  $234-238^\circ/760$  mm.,  $D^{15}_4$  0.987—0.988,  $[\alpha]_D + 45^\circ$ , which is best purified through its *hydrogen phthalate*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{C}_{11}\text{H}_{17}$ , m. p.  $124-125^\circ$ . If the alcohol is subjected to prolonged heating with alcoholic potassium

hydroxide, it gives an *ether*,  $O(CH_2 \cdot CH \cdot C_9H_{14})_2$ , b. p. 235—240°/25 mm.,  $D^{20}_D$  0.983. The alcohol,  $C_{11}H_{17} \cdot OH$ , when oxidised with potassium permanganate in the presence of aqueous sodium carbonate, gives camphenylone, hydroxycamphenylanic acid, and oxalic acid. In the presence of sodium hydroxide, the products of oxidation are camphenylone, camphenecamphoric acid, and oxalic acid. By a similar study of the oxidation of camphene, it is shown that the endocyclic transposition is not due to the permanganate, but rather to the isomerising action of the free alkali used in excess. Certain derivatives of camphenylidene-6-ethanol have been prepared. It gives a *diphenylurethane*, difficult to purify, and a *pyruvate*, b. p. 150—155°/10 mm., giving a *semicarbazone*, m. p. 167°. The ether,  $(C_{11}H_{17})_2O$ , when oxidised by sodium dichromate and sulphuric acid, gives first an aldehyde, and then camphenylidene-ethanoic acid.

A *chloride*,  $C_{11}H_{17}Cl$ , corresponding with camphenylidene-6-ethanol, may be obtained either by the action of hydrogen chloride on the alcohol in toluene solution at 140—150°, or by the action of phosphorus pentachloride either on the alcohol or the corresponding ether. This chloride has b. p. 100—102°/6 mm., 110°/15 mm.,  $D^{15}_D$  1.020,  $[\alpha]_D + 27.38^\circ$ . On oxidation with potassium permanganate, it yields camphenylone. Unlike  $\omega$ -chlorocamphene, it is oxidised by sodium dichromate and sulphuric acid, giving first an aldehyde and then camphenylideneacetic acid. The chloride is quite stable towards either hydrogen chloride or hydrogen bromide, undergoing no transposition. Further, it is not reduced by sodium in absolute alcohol, but under these conditions simply gives an *ethyl ether*,  $C_{10}H_{17} \cdot OEt$ , b. p. 125—130°/8 mm., 230°/760 mm. This ether, when oxidised by the chromic acid mixture gives camphenylideneacetic acid. If the reduction of the chloride is carried out by zinc and hydrochloric acid, the product is  $\omega$ -*methylcamphene*, b. p. 178°,  $D^{15}_D$  0.884,  $[\alpha]_D + 4.28^\circ$ . The chloride,  $C_{11}H_{17}Cl$ , when acted on by sodium or magnesium in anhydrous ether, gives a *terpene hydrocarbon*,  $C_{11}H_{17} \cdot C_{11}H_{17}$ , b. p. 210°/25 mm.,  $D^{15}_D$  0.952,  $[\alpha]_D + 67.30^\circ$ , which is remarkably stable towards aqueous potassium permanganate. By the action of sodium ethoxide, the chloride yields the corresponding ether,  $(C_{11}H_{17})_2O$ , described above. With sodium cyanide, the chloride yields the *nitrile*,  $C_{11}H_{17} \cdot CN$ , b. p. 140°/12 mm.,  $D^{15}_D$  0.959,  $D^{20}_D$  0.963,  $[\alpha]_D + 61.20^\circ$ , which is readily oxidised to camphenylone, and on hydrolysis gives the corresponding *acid*,  $C_{11}H_{17} \cdot CO_2H$ , m. p. 100°.

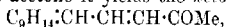


b. p.  $185^{\circ}/24$  mm.,  $[\alpha]_D + 41.16^{\circ}$ . From its behaviour on oxidation, it is suggested that this acid is really a mixture of two  $\alpha$ - and  $\beta$ -isomerides (see formulæ on previous page). When camphenylidene-6-ethanol is oxidised by Beckmann's mixture in the cold, it yields *camphenylidene-6-acetaldehyde*,  $C_9H_{14} \cdot CH \cdot CHO$ , b. p.  $130^{\circ}/12$  mm.,  $124^{\circ}/8$  mm.,  $D^{16}_D 1.002$ ,  $[\alpha]_D + 72.58^{\circ}$ , which gives a sodium bisulphite compound, a *semicarbazone*, m. p.  $233^{\circ}$ , and an *oxime*, b. p.  $160^{\circ}/15$  mm. The oxime gives a *hydrochloride*, and on dehydration yields *camphenylideneacetonitrile*,  $C_9H_{14} \cdot CH \cdot CN$ , b. p.  $132^{\circ}/6$  mm.,  $140^{\circ}/10$  mm.,  $D^{15}_D 0.987$ ,  $D^{20}_D 0.983$ ,  $[\alpha]_D + 110^{\circ}$ , which when boiled with alcoholic potassium hydroxide gives the corresponding *amide*,  $C_{16}H_{15} \cdot CO \cdot NH_2$ , m. p.  $192^{\circ}$ . This amide is very stable, and is not hydrolysed by sulphuric acid. Camphenylideneacetaldehyde gives a *diacetate*,  $C_9H_{14} \cdot CH \cdot CH(CO_2Me)_2$ , m. p.  $54-55^{\circ}$ .

If the oxidation of camphenylidene-6-ethanol with Beckmann's mixture is pushed further, the product is *camphenylideneacetic acid*, m. p.  $124-125^{\circ}$ , b. p.  $181^{\circ}/19$  mm., the same acid being obtained by the action of carbon dioxide on the magnesium derivative of  $\omega$ -bromocamphene. It gives an *ethyl ester*, b. p.  $150^{\circ}/22$  mm.,  $D^{30}_D 1.008$ , and an *acid chloride*, b. p.  $145^{\circ}/15$  mm., which by the action of ammonia is converted into the amide, m. p.  $192^{\circ}$  (see above). When heated on an oil-bath for several hours, camphenylideneacetic acid loses carbon dioxide and gives a *camphene*, m. p.  $45-46^{\circ}$ , b. p.  $158-160^{\circ}$ , which on oxidation yields camphor. On oxidation with potassium permanganate, the acid yields camphenylone, and on reduction with sodium in amyl alcohol it gives *isocamphanecarboxylic acid*, which when oxidised gives *r-camphenylanic acid*, m. p.  $75-76^{\circ}$ .

$\omega$ -Methylcamphene may be obtained by the reduction of camphenylideneacetaldehyde by zinc and hydrochloric acid, its constitution being shown by its behaviour on oxidation with potassium permanganate, when it yields camphenylone, oxalic acid, and camphenecamphoric acid. It is not oxidised by sodium dichromate and sulphuric acid, or by hydrogen chloride, but with hydrogen bromide it gives a *hydrobromide*,  $C_{11}H_{18}Br$ , b. p.  $108-110^{\circ}/17$  mm.,  $D^{15}_D 1.175$ .

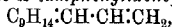
Camphenylideneacetaldehyde is capable of condensing with ketones. Thus with acetone it yields the *ketone*,



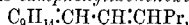
b. p.  $160^{\circ}/12$  mm.,  $D^{15}_D 0.980$ , giving a *semicarbazone*, m. p.  $220-221^{\circ}$ . With methyl ethyl ketone the aldehyde gives the *ketone*,  $C_9H_{14} \cdot CH \cdot CH \cdot CH \cdot COEt$ , b. p.  $172-175^{\circ}/12$  mm.,  $D^{15}_D 0.968$ , giving a *semicarbazone*, m. p.  $209-210^{\circ}$ . Owing to the presence of three conjugated double linkings, neither of these ketones is oxidised by chromic acid mixture, and the first-named is not acted on by hypochlorites. Camphenylideneacetaldehyde also reacts with magnesium alkyl haloids of low molecular weight to give unstable secondary alcohols, which, when distilled in a vacuum, give diethylenic hydrocarbons. Thus, with magnesium methyl



iodide, the final product is *camphenyldienepropylene*,



b. p. 85—90°/10 mm., 203—205°/760 mm.,  $D^{15}_D$  0.921,  $D^{20}_D$  0.917,  $[\alpha]_D + 76.39^\circ$ . With magnesium ethyl bromide the product is *camphenyldienebutylene*,  $\text{C}_9\text{H}_{14}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHMe}$ , b. p. 95—97°/12 mm. and 230—232°/760 mm.,  $D^{15}_D$  0.919,  $[\alpha]_D + 70^\circ$ . With magnesium propyl bromide the product is *camphenyldienepentene*,  $\text{C}_9\text{H}_{14}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHEt}$ , b. p. 110—120°/15 mm. and 238—240°/760 mm.,  $D^{15}_D$  0.905,  $[\alpha]_D + 80^\circ$ , and with magnesium butyl bromide the product is *camphenyldienehexene*,



b. p. 140°/10 mm. and 255°/760 mm.,  $D^{15}_D$  0.900,  $[\alpha]_D + 73.5^\circ$ . All these diethylenic hydrocarbons when oxidised with chromic acid mixture give the original aldehyde or camphenyldieneacetic acid. They also undergo spontaneous oxidation, giving camphenyldieneacetaldehyde and formaldehyde, acetaldehyde, propaldehyde, and butaldehyde respectively.

W. G.

**Chemistry of the Terpenes. XIX. Synthesis of a *m*-Menthadiene from *m*-*iso*-Cymene.** GEORGE GERALD HENDERSON and THOMAS FREDERICK SMEATON (T., 1920, 117, 144—149).

**Occurrence of the Terpene Terpinene in the Oil of *Eucalyptus megacarpa*.** HENRY G. SMITH (*J. Proc. Roy. Soc., N.S. Wales*, 1918, 52, 529—533).—The oil of *Eucalyptus megacarpa* contains pinene, limonene, and dipentene, about 30% of cineole, and possibly as much as 10% of terpinene. The latter was detected in the fraction boiling from 170—190° by the formation of its nitrosite, m. p. 155°, and by its rapid oxidation in the cold with Beckmann's chromic acid mixture, as evidenced by the increased optical rotation of the residual oil (consisting mainly of limonene) after the removal of the inactive terpinene.

G. F. M.

**The Vulcanisation of Caoutchouc with Agents other than Sulphur.** HENRY P. STEVENS (*J. Soc. Chem. Ind.*, 1917, 35, 107).

—Vulcanisation of caoutchouc with from 1 to 4% of dinitrobenzene or trinitrobenzene at 140° is possible in the additional presence of a considerable proportion (for example, 8 to 30%) of lead oxide or magnesium oxide; the trinitro-compound is more effective than its dinitro-analogue, whilst with nitrobenzene itself satisfactory results are not obtainable. The nitro-compound enters almost entirely into combination with the caoutchouc, and is not removable by acetone. The products possess poor mechanical qualities relative to caoutchouc vulcanised in the ordinary way with sulphur. Benzoyl peroxide also effects vulcanisation, and in this case no third substance is necessary; from 4 to 6% of the peroxide is required, and a vulcanisation period of ten to fifteen minutes at 130—135°. The products are weak and have a remarkably pale colour. [See also Bunschoten, A., 1918, i, 503; Ostromisslenski, A., 1916, i, 278.]

D. F. T.

**The Nature of Vulcanisation. I. The Combination of Rubber with Sulphur. II. The Action of Solvents on Vulcanised Rubber.** H. P. STEVENS (*J. Soc. Chem. Ind.*, 1919, 38, 192—196r).—The results on which Harries and Fonrobert (A., 1916, i, 659, 733) base their opinion that vulcanisation of caoutchouc is essentially a physical process, and may occur without any appreciable combination with sulphur, are probably explained by unsuitable conditions of experiment. Under similar conditions, but with the additional precaution of vulcanising the mixture of caoutchouc and sulphur in thin sheets, so as to ensure greater uniformity of heating, and consequently of vulcanisation, the author obtained a product which, after exhaustive extraction with acetone, retained more than 1% of combined sulphur. It is therefore not possible to effect ordinary vulcanisation without the concurrent fixation of an appreciable proportion of sulphur. With an increasing proportion of combined sulphur, caoutchouc becomes less and less soluble in solvents such as benzene; freshly vulcanised samples containing 0.27% and 0.39% of combined sulphur could be dissolved in benzene, whereas 0.45% prevented solution; after storage for three months, none of these samples would pass completely into solution. The extract obtained on treating more highly vulcanised caoutchouc with hot benzene contains the same proportion of combined sulphur as the undissolved residue.

D. F. T.

**Autoxidation of Colophony.** LUDWIG PAUL (*Kolloid Zeitsch.*, 1919, 25, 241—246).—The constituents of colophony are investigated, and some of the products examined and characterised. When a solution of colophony in alkali is treated with hydrochloric acid, a voluminous precipitate of  $\gamma$ -pinic acid is obtained; this substance has m. p. 75—76°, which in eight months rises to about 88°.  $\alpha$ -Pinic acid has a constant m. p. 81—83°, and shows a tendency to form liquid crystals. It is soluble in water and petroleum, as also is  $\gamma$ -pinic acid.  $\beta$ -Pinic acid melts at 98—100° (compare A., 1918, i, 411).

J. F. S.

**Compounds of High Molecular Weight. I. Synthesis of some Acylglucosides of High Molecular Weight.** SVEN ODRÉN (*Arkiv Kem. Min. Geol.*, 1917, 6, No. 18).—Almost all known organic compounds of high molecular weight are natural products of indefinite constitution and extremely difficult to purify, circumstances which are great obstacles to the study of their physico-chemical properties. The author has now synthesised a series of esters of 2:4:6-tribromophenol-*d*-glucoside with a view to a study of the variation of their properties with molecular weight. The esters were prepared by E. Fischer's process, for which the most suitable conditions in this case consist in treating a suspension of the finely divided glucoside in dry chloroform with excess (about one-third) of the acid chloride and quinoline at about 50°. The product was usually isolated by precipitation from the solution by

alcohol, and purified by repetition of the treatment, the bromine content furnishing an effective criterion of purity. The constancy of melting point of the products renders it improbable that the use of quinoline caused any stereoisomeric change during the reaction. All the products were stable, indifferent substances, and slightly laevorotatory. With the exception of the tetrapropionate, the tetrabenzoate, and the tetra-*p*-bromobenzoate, which are crystalline, they were amorphous substances resembling stearin or fats, and in their aspect and solubility relationships lipid in character. It is noteworthy that the tetrabenzoate exists in two interconvertible forms, an amorphous form, m. p. 94°, and a crystalline, m. p. 147°, the difference in m. p. being apparently conditioned by the variation in granular size (compare Pawlov, A., 1910, ii, 1033).

The following derivatives of 2:4:6-tribromophenol-*d*-glucoside are described: the *tetra*-acetate,  $C_{29}H_{21}O_{10}Br_3$ , needle-shaped crystals, m. p. 195–196°; the *tetrapropionate*,  $C_{24}H_{29}O_{10}Br_3$ , prisms, m. p. 89.5°; the *tetralaurate*,  $C_{60}H_{107}O_{10}Br_3$ , resembling fat, m. p. 48–49°; the *tetramyristate*,  $C_{68}H_{117}O_{10}Br_3$ , m. p. 56–57°; the *tetrapalmitate*,  $C_{76}H_{133}O_{10}Br_3$ , resembling stearin, m. p. 61–62°; the *tetrestearate*,  $C_{84}H_{149}O_{10}Br_3$ , resembling stearin, m. p. 70–71°, in tetrachloroethane solution,  $[\alpha]_D^{20} -3.6^\circ$ ; the *tetrahexabromostearate*,  $C_{84}H_{125}O_{10}Br_{27}$ , fairly hard, m. p. 152°; the *tetracerotate*,  $C_{116}H_{213}O_{10}Br_3$ , solid, m. p. 80–81°; the *tetrabenzoate*,  $C_{40}H_{29}O_{10}Br_3$ , m. p. as above; the *tetra-p*-bromobenzoate,  $C_{40}H_{25}O_{10}Br_7$ , m. p. 115° amorphous, 214° crystalline (aggregates of needle-shaped crystals); the *tri-β*-naphthoate,  $C_{45}H_{31}O_9Br_3$ , m. p. 175°; the *tetra-β*-naphthoate,  $C_{56}H_{37}O_{10}Br_3$ , m. p. 218°.

In addition, the following were prepared from  $\alpha$ -methyl-*d*-glucoside: the *tripalmitate*,  $C_{55}H_{104}O_9$ , amorphous, m. p. 77°; the *tristearate*,  $C_{61}H_{108}O_9$ , amorphous, m. p. 82°; the *tetrestearate*,  $C_{79}H_{150}O_{10}$ , amorphous, m. p. 68°; the *tetra-p*-bromobenzoate,  $C_{35}H_{26}O_{10}Br_4$ , needles, m. p. 148°.

J. K.

### Compounds of High Molecular Weight. II. Some Acyl Derivatives of Natural Glucosides of High Molecular Weight.

SVEN ODÉN (*Arkiv Kem. Min. Geol.*, 1918–1919, 7, No. 15, 1–22).—The method of acylation previously described (see previous abstract) gives good results when applied to natural glucosides, and has the advantage over older methods of giving completely acylated products. In several cases the products were crystalline, with a sharp melting point, but the granular size was again observed to have a distinct influence on the melting point; in all cases this was depressed by precipitation of the amorphous or microcrystalline form by alcohol from a solution of the crystalline form in chloroform. The chlorides of  $\beta$ -naphthalene- and  $\alpha$ -bromocamphor- $\pi$ -sulphonic acids were also used, this being the first occasion on which sulpho-derivatives of members of the sugar group have been prepared. In these cases, however, a temperature above 50° was necessary for the condensation, the reaction proceeded less smoothly,

the resulting compounds were impure, and the yields only about 30%. The products were very friable, and appeared under the microscope as small, strongly refractive, glassy spheres. In the impure condition, they are not dissimilar from the oxidation products of sulphite liquors. The following derivatives are described.

*Salicin*:—*pentacinnamate*,  $C_{58}H_{49}O_{12}$ , needles, m. p.  $173^{\circ}$ ,  $[\alpha]_D^{19} + 46.5^{\circ}$ , *pentaphenylpropionate*,  $C_{58}H_{38}O_{12}$ , long needles, m. p.  $58^{\circ}$ ,  $[\alpha]_D^{19} - 3.5^{\circ}$ , and *penta-p-bromobenzoate*,  $C_{48}H_{33}O_{12}Br_5$ , needles, m. p.  $158^{\circ}$ ,  $[\alpha]_D^{19} + 30.2^{\circ}$ .

*Helicin*:—*tetracinnamate*,  $C_{49}H_{40}O_{11}$ , prisms, m. p.  $176^{\circ}$ ,  $[\alpha]_D^{18} + 77.3^{\circ}$  (*p-bromophenylhydrazone*,  $C_{55}H_{45}O_{10}N_2Br$ , amorphous, m. p.  $118-120^{\circ}$ , decomp.), *tetrapalmitate*,  $C_{77}H_{126}O_{11}$ , amorphous, m. p.  $68^{\circ}$  (*p-bromophenylhydrazone*,  $C_{83}H_{141}O_{10}N_2Br$ , amorphous, m. p. ca.  $45^{\circ}$ ).

*Coniferin*:—*pentacinnamate*,  $C_{61}H_{52}O_{13}$ , amorphous, m. p. ca.  $145^{\circ}$ , and *tetrestearate*,  $C_{88}H_{138}O_{12}$ , amorphous, m. p.  $69-70^{\circ}$ .

*Amygdalin*:—*heptabenzoate*,  $C_{69}H_{55}O_{18}N$ , small needles, m. p.  $218^{\circ}$ ,  $[\alpha]_D^{18} - 10.5^{\circ}$ , *hepta-p-chlorobenzoate*,  $C_{69}H_{48}O_{18}NCl_7$ , crystals, m. p.  $234^{\circ}$ , slightly levorotatory, *hepta-p-bromobenzoate*,

$C_{69}H_{48}O_{18}NBr_7$ , needles, m. p.  $229^{\circ}$ , *hepta-anisate*,  $C_{76}H_{68}O_{25}N$ , amorphous, m. p.  $117-119^{\circ}$ ,  $[\alpha]_D^{20} + 13.2^{\circ}$ , and *heptastearate*,  $C_{116}H_{265}O_{18}N$ , amorphous, m. p.  $92^{\circ}$ ,  $[\alpha]_D^{25} - 8.40^{\circ}$ .

*Phloridzin*:—*hepta-p-bromobenzoate*,  $C_{70}H_{45}O_{17}Br_7$ , amorphous, m. p.  $130-132^{\circ}$ ,  $[\alpha]_D^{19} + 19.5^{\circ}$ , and *heptapalmitate*,  $C_{133}H_{234}O_{17}$ , amorphous, m. p.  $51^{\circ}$ ,  $[\alpha]_D^{18} - 9.55^{\circ}$ .

*a-Methyl-d-glucoside*:—*tetra-β-naphthalenesulphonate*,  $C_{47}H_{36}O_{14}S_4$ , snow-white powder, m. p.  $147^{\circ}$ , *tetra-α-bromocamphor-π-sulphonate*,  $C_{47}H_{36}O_{18}Br_4S_4$ , glassy spheres, m. p.  $150^{\circ}$ ,  $[\alpha]_D^{19} + 128^{\circ}$ , and *tetrapalmitate*,  $C_{71}H_{134}O_{16}$ , needles, m. p.  $69^{\circ}$ ,  $[\alpha]_D^{18} + 46.9^{\circ}$ .

2 : 4 : 6-Tribromophenol-d-glucoside:—*tetra-α-bromocamphor-π-sulphonate*,  $C_{52}H_{65}O_{18}Br_4S_4$ , amorphous, m. p.  $181^{\circ}$ ,  $[\alpha]_D^{20} + 75.1^{\circ}$ .

All optical data refer to solutions in chloroform. J. K.

**Compounds of High Molecular Weight. III. Derivatives of Raffinose and of some other Sugar Derivatives of High Molecular Weight.** SVEN ODÉN (*Arkiv Kem. Min. Geol.*, 1918-1919, 7, No. 15, 23-38).—The eleven hydroxyl groups of raffinose render this compound a very suitable starting point for the synthesis of derivatives of high molecular weight. The method of acylation already described was successfully applied in this case, and gave completely acylated products (contrast Stollé, A., 1901, i, 189); but the reaction took place more slowly, and some material was always recovered unchanged; sulphonyl chlorides react still less readily than those of carboxylic acids. The products were all amorphous and definitely uniform, except possibly the hendeca-hexabromostearate. Amorphous derivatives were also obtained from saccharose, but mannitol and dulcitol furnished crystalline products. From inositol, only the hexa-p-bromobenzoate could be obtained. The following derivatives are described.

*Raffinose*:—*hendecabenzozate*,  $C_{85}H_{76}O_{27}$ , m. p.  $113^{\circ}$ ,  $[\alpha]_D^{20} + 106.8^{\circ}$ , *hendeca-p-chlorobenzozate*,  $C_{95}H_{65}O_{27}Cl_{11}$ , m. p.  $130-132^{\circ}$ , *hendeca-p-bromobenzozate*,  $C_{95}H_{65}O_{27}Br_{11}$ , m. p.  $136-138^{\circ}$ ,  $[\alpha]_D^{20} + 85.2^{\circ}$ , *hendecapalmitate*,  $C_{194}H_{362}O_{27}$ , m. p.  $53^{\circ}$ ,  $[\alpha]_D^{20} + 31.8^{\circ}$ , *hendecastearate*,  $C_{216}H_{406}O_{27}$ , m. p.  $62^{\circ}$ ,  $[\alpha]_D^{20} + 28.3^{\circ}$ , *hendecacerotate*,  $C_{204}H_{382}O_{27}$ , m. p.  $68^{\circ}$ , *hendecahexabromostearate*,  $C_{216}H_{340}O_{27}Br_{66}$ , m. p.  $147-148^{\circ}$ ,  $[\alpha]_D$  ca.  $+12^{\circ}$ , and *hendecanaphthalenesulphonate*,  $C_{128}H_{98}O_{38}S_{11}$ , m. p. ca.  $126^{\circ}$ .

*Sucrose*:—*octacinnamate*,  $C_{84}H_{70}O_{19}$ , m. p.  $87-88^{\circ}$ ,  $[\alpha]_D^{18} + 12.5^{\circ}$ , and *octa-p-bromobenzozate*,  $C_{68}H_{46}O_{19}Br_8$ , m. p.  $116-118^{\circ}$ ,  $[\alpha]_D + 27^{\circ}$ .

*Dulcitol*:—*hexa-p-chlorobenzozate*,  $C_{48}H_{32}O_{12}Cl_6$ , m. p.  $238^{\circ}$ , and *hexapalmitate*,  $C_{162}H_{194}O_{12}$ , m. p.  $74^{\circ}$ , both optically inactive.

*d-Mannitol*:—*hexa-p-bromobenzozate*,  $C_{48}H_{32}O_{12}Br_6$ , prisms, m. p.  $96^{\circ}$ ,  $[\alpha]_D^{18} + 29.6^{\circ}$ .

*Inositol*:—*hexa-p-bromobenzozate*,  $C_{48}H_{30}O_{12}Br_6$ , prisms, m. p.  $264^{\circ}$ , optically inactive.

All optical data refer to solutions in chloroform.

J. K.

**Diastereomeric Acyl Derivatives of some Sugars.** SVEN ODNÉN (*Arkiv Kem. Min. Geol.*, 1918—1919, 7, No. 16, 1—16).—The acylation of *d*-glucose by treatment with acid chlorides and quinoline required some days for completion at temperatures of  $30-70^{\circ}$ . In all cases, the product, corresponding in its sparing solubility in alcohol with those obtained in other instances (see preceding abstracts), was accompanied by an isomeride, easily soluble in alcohol, and differing in m. p. and specific rotation. The less soluble modifications were also obtained as sole products by the acylation of  *$\beta$* -*d*-glucose, usually at rather higher temperatures, and are therefore to be derived from  *$\beta$* -*d*-glucose, whilst the more soluble forms correspond with  *$\alpha$* -*d*-glucose. Similar results were obtained with *d*-galactose and *l*-arabinose. In these cases, the author designates the parent sugar, of which only one solid form is known, and that modification of the acylated sugar which is analogous in respect of melting point, specific rotation, and solubility. The following compounds are described: *penta-anisoyl-d-glucose*,  $C_{40}H_{42}O_{16}$ ,  *$\alpha$* -form, m. p.  $98^{\circ}$ ,  $[\alpha]_D^{19} + 103^{\circ}$ , and the  *$\beta$* -form, amorphous, m. p.  $175^{\circ}$ ,  $[\alpha]_D^{20} + 11^{\circ}$ ; *penta-p-nitrobenzoyl-d-glucose*,  $C_{41}H_{27}O_{15}N_5$ ,  *$\alpha$* -form, m. p.  $235^{\circ}$  (decomp.),  $[\alpha]_D^{19} + 176^{\circ}$ , soluble in chloroform, and the  *$\beta$* -form, m. p. ca.  $265^{\circ}$  (decomp.), insoluble in chloroform; *penta-p-bromobenzoyl-d-glucose*,  $C_{41}H_{27}O_{11}Br_5$ ,  *$\alpha$* -form, crystals, m. p.  $197^{\circ}$ ,  $[\alpha]_D + 110^{\circ}$ , and the  *$\beta$* -form, amorphous, m. p.  $220^{\circ}$ ,  $[\alpha]_D^{18} + 83^{\circ}$ ; *penta-p-bromobenzoyl-d-galactose*,  $C_{41}H_{27}O_{11}Br_5$ ,  *$\alpha$* -form, needles, m. p.  $130^{\circ}$ ,  $[\alpha]_D + 45^{\circ}$ , and the  *$\beta$* -form, prisms, m. p.  $267.5^{\circ}$ ,  $[\alpha]_D + 107^{\circ}$ ; *tetra-p-bromobenzoyl-l-arabinose*,

$C_{33}H_{22}O_9Br_4$ ,  *$\alpha$* -form, m. p.  $205^{\circ}$ ,  $[\alpha]_D^{20} + 383^{\circ}$ , and the  *$\beta$* -form, m. p.  $118^{\circ}$ ,  $[\alpha]_D^{20} + 228^{\circ}$ ; *hexa-p-nitrobenzoyldulcitol*,  $C_{48}H_{32}O_{24}N_6$ , crystals, m. p.  $265-268^{\circ}$ ; *octa-p-nitrobenzoylsucrose*,  $C_{68}H_{46}O_{35}N_8$ , amorphous, m. p.  $150^{\circ}$  (decomp.); *tetra-p-nitrobenzoyl-2:4:6-tribromophenol-d-glucoside*,  $C_{40}H_{25}O_{13}N_4Br_3$ , amorphous, m. p.  $247^{\circ}$ ,  $[\alpha]_D - 39^{\circ}$ ;

and *tetrapalmityl-l-arabinose*,  $C_{66}H_{134}O_9$ , amorphous, m. p.  $69.5^\circ$ ,  $[\alpha]_D^{20} + 4^\circ$ .

All optical data refer to solutions in chloroform.

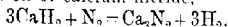
J. K.

**The Theory of Colour Lakes.** C. BRENNER (*Helv. Chim. Acta* 1920, 3, 90—103).—See this vol., ii, 194.

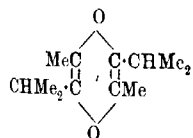
**Catalytic Reduction of Furfuraldehyde.** HANS PRINGSHEIM and HARTMUT NOTH (*Ber.*, 1920, 53, [B], 114—118).—The hydrogenation of furfuraldehyde has already been studied by Padoa and Ponti (A., 1907, i, 146), and that of furan by Bourguignon (A., 1908, i, 280). A new study of this subject has now supplied a connecting link between the earlier results. By arranging that the furfuraldehyde is exposed to the reduced nickel as much as possible, the authors have obtained furan, 1-methylfuran, and a dihydrofuran, besides the products described by Padoa and Ponti. It appears, therefore, that the hydrogenation of furfuraldehyde proceeds in three ways concurrently: (I) reduction of the aldehyde group as far as methyl, and then hydrogenation of the ring; (II) expulsion of the aldehyde group with the formation of furan, and further hydrogenation; and (III) rupture of the ring and formation of pentan- $\beta$ -ol and methyl propyl ketone. J. C. W.

**Some Reactions of Calcium Hydride.** SIGISMOND REICH and H. O. SERPEK (*Helv. Chim. Acta*, 1920, 3, 138—144).—The present investigation was undertaken on account of the importance of calcium hydride as a reducing agent, particularly in organic chemistry, and also because the data recorded by Moissan, by Erdmann and van der Smitten (A., 1908, ii, 587), and by Mayer and Altmayer (A., 1908, i, 845) are discordant in many respects.

Carbon monoxide is reduced by calcium hydride heated to dull redness, with the formation of hydrogen, methane, and formaldehyde, rather more than 16% of the carbon monoxide being converted into the latter. When a mixture of the hydride with sodium hydrogen carbonate is gently heated, formic acid is produced, the yield being 13.2% of that theoretically possible; a similar result is obtained when normal sodium carbonate is used. Ammonia is formed in small amount when nitrogen is passed over calcium hydride at about  $500^\circ$ , but the main reaction appears to consist in the formation of calcium nitride.



Acetone reacts energetically with finely divided calcium hydride,



giving mesityl oxide, b. p.  $128-130^\circ$ , and the substance (annexed formula), b. p.  $226-236^\circ$ ; acetophenone also yields condensation products with calcium hydride at  $240^\circ$ , but these have not been fully investigated.

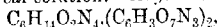
Quinoline is converted at  $220^\circ$  into  $\beta\beta$ -diquinolyl, needles, m. p.  $190^\circ$ , whilst pyridine at  $160-165^\circ$  yields a small quantity of crystalline matter,

m. p. 54—56°, which does not appear to be identical with any known dipyrrolyl.

Other organic compounds, such as ethyl acetate, benzene, nitrobenzene, and anthraquinone, did not appear to react with calcium hydride under varying conditions of temperature. Calcium hydride, therefore, only appears to react as a reducing agent at very high temperatures, and its use in the hydrogenation of organic compounds must be very limited, the more so since its action, when it does occur, appears to lead preferably to condensations.

When calcium hydride is added to an ethereal solution of ferric chloride, hydrogen is evolved, and a brown precipitate is produced which is soluble in water to an acid solution; its composition is represented by the formula  $\text{Ca}_3\text{FeCl}_3(\text{C}_6\text{H}_6\text{O})_3$ . H. W.

**Dipicrates of Arginine and Histidine.** L. HUGOUNENQ and G. FLORENCE (*Bull. Soc. Chem. Biol.*, 1919, 1, 102—106).—The dipicrates have been prepared by the action of picric acid on the monopicrates in ethereal solution. *Arginine dipicrate*,



m. p. 156° (corr.), forms spherules of fine needles, and *histidine dipicrate*,  $\text{C}_6\text{H}_9\text{O}_2\text{N}_3(\text{C}_6\text{H}_3\text{O}_7\text{N}_3)_2 \cdot 5\text{H}_2\text{O}$ , long needles, m. p. 80°.

J. C. D.

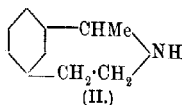
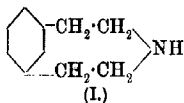
**Synthesis of some Purine Glucosides.** BURCKHARDT HELFERICH and MALTE VON KÜHLEWEIN (*Ber.*, 1920, 53, [B], 17—22. Compare Fischer and Helferich, A., 1914, i, 333).—By the interaction of the silver salts of purines with acetobromogalactose and acetobromoarabinose, followed by hydrolysis of the acetates with methylalcoholic ammonia, further purine-glucosides have been obtained, as follows. *Tetra-acetyltheophylline-d-galactoside*,  $\text{C}_7\text{H}_7\text{O}_3\text{N}_4\text{C}_6\text{H}_7\text{O}_3\text{Ac}_4$ , has m. p. 135—137° (corr.).  $[\alpha]_D^{20} - 13.97^\circ$ , 12.96°, in toluene, and *theophylline-d-galactoside* forms long needles, m. p. 251° (corr.; decomp.).  $[\alpha]_D^{20} + 23.45^\circ$ , in water. *Tetra-acetyltheobromine-d-galactoside* crystallises in microscopic needles, m. p. 208° (decomp.).  $[\alpha]_D^{20} + 9.76^\circ$ , in chloroform, and *theobromine-d-galactoside* forms minute needles with  $2\text{H}_2\text{O}$ , decomp. above 150°, and is very speedily decomposed by water. *Triacetyltheophylline-l-arabinoside* forms thin, rhombic plates, m. p. 214—216°,  $[\alpha]_D^{20} + 43.34^\circ$ , in *s*-tetrachloroethane, and *theophylline-l-arabinoside* crystallises in slender needles, m. p. 276—277°,  $[\alpha]_D^{20} + 34.08^\circ$ , in water. J. C. W.

**The Condensation of Ethyl Acetoacetate with *p*-Dimethylaminobenzaldehyde and Ammonia.** LEONARD ERIC HINKEL and HERBERT WILLIAM CREMER (T., 1920, 117, 137—140).

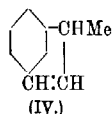
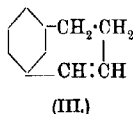
**Influence of Hydrogen-ion Concentration on the Volatility of Indole from Aqueous Solution.** HARPER F. ZOLLER (*J. Biol. Chem.*, 1920, 41, 37—44).—The range of most rapid volatilisation of indole from the aqueous solutions studied is from  $p_H$  8.0 to 10.5. This has led to the adoption of direct distillation in the separation of indole (this vol., ii, 203). J. C. D.

**Ring Closure in the Meta-position in the Benzene Series.**

**II. Reduction of *m*-Xylylene Dicyanide.** JULIUS VON BRAUN, (FRL.) L. KARPFF, and W. VON GARN (*Ber.*, 1920, **53**, [B], 98—109. Compare this vol., i, 87).—When *m*-xylylene dicyanide is reduced by means of sodium in alcohol, the normal product, the primary diamine, forms only about one-seventh of the yield. The chief product is a saturated, secondary amine of the formula (I) or (II).



It yields isophthalic acid on oxidation, and the quaternary ammonium hydroxide obtained from it after treatment with methyl iodide loses, not only water, but also dimethylamine on distillation, giving an unsaturated hydrocarbon, (III) or (IV). This may



be reduced to a saturated hydrocarbon, and both compounds yield isophthalic acid on oxidation. This result indicates, therefore, that, contrary to all experience, the two meta-carbon atoms in the benzene ring may be connected, not only by a chain containing nitrogen, but by a simple carbon chain also.

*m*-Di-*β*-aminoethylbenzene,  $C_6H_4(CH_2 \cdot CH_2 \cdot NH_2)_2$ , is a colourless liquid with b. p. 165—170°/20 mm. It absorbs carbon dioxide from the air, forms a *dihydrochloride*, m. p. 290°, a *platinichloride*, m. p. 238°, and a *picrate*, m. p. 238°. Unlike the corresponding diamine of the ortho-series (A., 1917, i, 130), it reacts with methyl iodide to form a *bisquaternary iodide*,  $C_6H_4(CH_2 \cdot CH_2 \cdot NMe_3I)_2$ , m. p. 212°.

The secondary amine, (I) or (II), has b. p. 97—98°/16 mm., and forms a *hydrochloride*, m. p. 160°, a *platinichloride*, m. p. 232°, a sulphur-yellow *picrate*, m. p. 176°, a *benzoyl* derivative, leaflets, m. p. 72°, a *phenylthiocarbamide*,  $C_{10}H_{12}N \cdot CS \cdot NHPh$ , leaflets, m. p. 87°, an oily *nitroso*-compound, and a *quaternary methiodide*,  $C_{10}H_{12}NMe_3I$ , leaflets, m. p. 236° (corresponding *chloride*, and *platinichloride*,  $C_{22}H_{30}N_2Cl_6Pt$ , m. p. 238°). It also reacts with *o*-xylylene dibromide to form the compound,  $C_{10}H_{12}N \begin{smallmatrix} CH_2 \\ | \\ Br \\ | \\ CH_2 \end{smallmatrix} C_6H_4$ ,

m. p. 168—169°. The unsaturated hydrocarbon, (III) or (IV), is a mobile liquid with intense, characteristic odour. b. p. 62—63°/18 mm.,  $D_4^{20}$  0.900 (unusually low compared with the isomeric hydrocarbons,  $C_{10}H_{10}$ ),  $n_D^{20}$  1.54029. It polymerises like styrene, and forms a *dibromide*, m. p. 48°. On reduction by means of colloidal



palladium, it yields the *hydrocarbon*,  $C_{10}H_{12}$ , which is a mobile liquid with pleasant odour and abnormally low density, b. p.  $50.5-51.5^\circ/14$  mm.,  $D_4^{25}$  0.852,  $n_D^{25}$  1.4968. J. C. W.

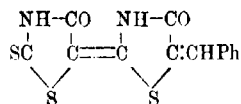
**Preparation of 3:6-Diaminoacridine.** POULENC FRÈRES and ROBERT MEYER (Brit. Pat. 137214).—*m*-Phenylenediamine is melted at  $130^\circ$  with formic acid, or oxalic acid and glycerol, or other polyhydric alcohol, and a condensing agent such as anhydrous zinc or calcium chloride; when the evolution of carbon dioxide has ceased, the temperature is raised to, and maintained for two hours at,  $150-170^\circ$ , and the diaminoacridine is isolated from the resultant, almost solid mass by treatment with water and ammonia. It may be purified through its sulphate, which is sparingly soluble in very dilute sulphuric acid. [See, further, *J. Soc. Chem. Ind.*, 1920, March.] G. F. M.

**Rhodanines.** CH. GRÄNACHER (*Helv. Chim. Acta*, 1920, 3, 152-163).—The author has attempted to elucidate the constitution of Nencki's rhodanine red, but great difficulty has been experienced in purifying the dye, since it could not be caused to crystallise; analyses of the product, moreover, show it to be more complex than was anticipated. It has, however, been shown that the imino-hydrogen of the rhodanine is not concerned with its oxidation by ferric chloride, since *N*-substituted rhodanines, such as 3-phenylrhodanine, also yield red dyes under suitable conditions. On the other hand, benzylidenerhodanine is not affected by ferric chloride, so that the presence of a free methylene group appears essential to the production of a dye.

Rhodanine appears to be tautomeric with 4-hydroxy-2-thiothiazole, since it can be readily transformed in alkaline solution into the colourless benzoyl derivative,  $S \begin{smallmatrix} \text{C(SBz)N} \\ \text{CH}=\text{C}\cdot\text{OBz} \end{smallmatrix}$ , whilst if the

methylene hydrogen atoms are substituted, as in benzylidenerhodanine, the yellow monobenzoyl derivative,  $S \begin{smallmatrix} \text{C(SBz)=N} \\ \text{C}(\text{:CHPh})\cdot\text{CO} \end{smallmatrix}$

is produced. Alkylidenerhodanines react with aniline and phenylhydrazine to yield the corresponding phenylhydrazones and anilides, the sulphur of the thio-keto-group being removed as hydrogen sulphide. Since aniline is comparatively readily removed from these anilides, they can be employed for condensing the rhodanine molecule with compounds containing a reactive methylene group; in this manner, benzylidenerhodanineanilide can be condensed with a second molecule of rhodanine to yield 5-benzylidene-5'-rhodanylidene-2-rhodanine (annexed formula). Reaction with aniline or phenylhydrazine proceeds in a totally different manner with rhodanines, such



as *N*-phenylrhodanine, which contain the free methylene group; in

this case, the sulphur of the thio-keto-group remains unaffected, and complete fission of the rhodanine ring occurs, with formation of thiocarbamides or thiosemicarbazides, reaction occurring so readily that the process is conveniently used for the preparation of the latter class of substances.

The following individual substances are described: *dibenzoyl-rhodanine*, colourless needles, m. p. 126°; *5-benzylidene-2-benzoyl-mercaptothiazoline*, deep yellow leaflets, m. p. 151—152°; *5-benzylidenerhodanine-2-phenylhydrazone*, orange-red leaflets, m. p. 219° after softening at 210°; *5-p-dimethylaminobenzylidenerhodanine-2-phenylhydrazone*, red leaflets, m. p. 282° (decomp.); *5-benzylidenerhodanine-2-anilide*, pink leaflets, m. p. 252—253° after softening at 248°; *5-p-dimethylaminobenzylidenerhodanine-2-anilide*, dark yellow leaflets, m. p. 308° (hydrolysis of the two substances last named leads to the formation of 2:4-diketo-5-benzylidenethiazolidine,  $\begin{array}{c} \text{CO-S} \\ \text{NH-CO} \end{array} > \text{C:CHPh}$ , m. p. 238—240°, and of 2:4-diketo-5-p-dimethylaminobenzylidenethiazolidine, long, orange-yellow needles, m. p. 296°, respectively); *5-benzylidene-5'-rhodanylidene-2-rhodanine*, brown leaflets; *diphenylthiocarbamide*, colourless leaflets, m. p. 151—152°; *diphenylthiosemicarbazide*, long, colourless needles, m. p. 176—177°.

H. W.

**Acyl Substituted isoThiohydantoin.** AUGUSTUS EDWARD DIXON and RAYMOND THOMAS JOACHIM KENNEDY (T., 1920, 117, 74—79).

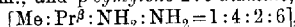
***p*-Cymylene-2:6-diamine and the Formation of 2:4-Dinitrotoluene by the Nitration of *p*-Cymene.** J. ALFTHAN (Ber., 1920, 53, [B], 78—98).—With a view to the utilisation of the large quantities of *p*-cymene which accumulate in the sulphite-cellulose industry (1 kilo. per ton of cellulose). Aschan has studied the nitration of the hydrocarbon (*Finska Kemistsamfundets Meddelanden*, 1916, 25, 122). The conditions finally adopted, and now described, are the gradual addition of one part of cymene to a mixture of two parts of nitric acid (D 1.5) and four parts of sulphuric acid (1.84), the temperature being kept below 0°. The main product is a crude dinitro-derivative, which may be reduced to a crude diamine. When this is examined, it is found to consist of some 2:4-tolylenediamine, but chiefly *p*-cymylene-2:6-diamine, a new base. The occurrence of the toluene derivative therefore suggests that 2:4-dinitrotoluene is present in the nitration product, the isopropyl group having been expelled by a nitro-group. The mechanism of this displacement is discussed, but various probable suggestions are negatived by experience, and the question is left open. There also seems to be little hope of making the dinitrotoluene the main product, and so utilising cymene as a source of trinitrotoluene.

The separation of the products of nitration is a difficult matter,

k\*

distillation under reduced pressure being the best method. The crude product is partly oily and partly solid, the latter yielding 2:4-dinitrotoluene, m. p.  $70^{\circ}$ , b. p. below  $161^{\circ}/6$  mm., and 2:6-dinitro-*p*-cymene, m. p.  $54^{\circ}$ , b. p.  $161$ — $163^{\circ}/6$  mm. The oil contains, in addition, cymene, *p*-tolyl methyl ketone, and a mononitrocymene, which can be converted into the above dinitrocymene. The crude dinitro-compounds are reduced by means of tin and zinc and hydrochloric acid (tin at the commencement, zinc after the reaction has set in), and the crude diamines separated by fractional distillation under 15 mm. pressure.

2:4-Tolylenediamine, purified by crystallisation from benzene, forms pale yellow, very hard needles, m. p.  $98$ — $99^{\circ}$ , b. p.  $160$ — $168^{\circ}/15$  mm., and *p*-cymylene-2:6-diamine,



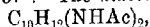
separates from 20% alcohol in glistening, thin leaflets, m. p.  $95$ — $96^{\circ}$ , b. p.  $300$ — $300.5^{\circ}/768$  mm.,  $158$ — $162^{\circ}/10$  mm., 0.7469 gram dissolving in 100 grams of water at  $25^{\circ}$ . The following salts of *p*-cymylene-2:6-diamine are described: *hydrochloride*, needles, decomp.  $180$ — $200^{\circ}$ ; characteristic *zincchloride*,



pale pink needles, decomp. above  $245^{\circ}$ ; *hydrogen sulphate*,

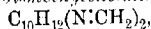


decomp.  $250^{\circ}$ ; *nitrate*, long leaflets, decomp.  $170^{\circ}$ ; *hydrogen oradate*,  $\text{B}_2\text{H}_2\text{C}_2\text{O}_4$ , rods, m. p.  $188$ — $189^{\circ}$  (decomp.); and *thiocyanate*, needles, m. p.  $137^{\circ}$ . The *diacetyl* derivative,

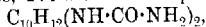


crystallises in thin needles, m. p.  $254^{\circ}$ , and yields a 3-nitro-compound, needles, m. p.  $280$ — $282^{\circ}$ , which may be hydrolysed to 3-nitro-*p*-cymylene-2:6-diamine, yellow needles, m. p.  $187^{\circ}$ . The *dibenzoyl* derivative forms needles, m. p.  $246$ — $247^{\circ}$ .

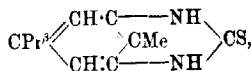
Condensation products of the cymylenediamine are as follows: with formaldehyde, 2:6-bismethyleneimino-*p*-cymene,



m. p.  $170$ — $180^{\circ}$  (decomp.); from the chloride and potassium cyanate or thiocyanate, 2:6-dicarbamido-*p*-cymene,



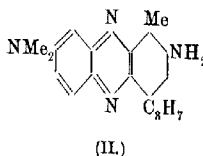
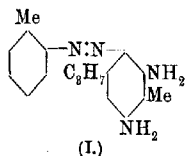
needles, m. p.  $270$ — $280^{\circ}$  (decomp.), and 2:6-dithiocarbamido-*p*-cymene, m. p.  $165$ — $175^{\circ}$  (decomp.); with carbon disulphide and alcoholic potassium hydroxide, 2-methyl-5-isopropyl-1:3-phenylene-thiocarbamide,



m. p.  $157$ — $158^{\circ}$ ; and with alcoholic oxalic acid, *m-aminocymyloramic acid*,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_{12}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , m. p.  $217$ — $218^{\circ}$  (decomp.).

The following dyes have also been prepared: a dark red *hydroxynazo-dye*,  $\text{C}_{30}\text{H}_{22}\text{O}_{14}\text{N}_4\text{S}_4\text{Na}_4$ , by diazotising at a low temperature, to avoid the production of a Bismarck-brown, and coupling with sodium  $\beta$ -naphthol-3:6-disulphonate; a *chrysoidine* of the

formula (I), reddish-yellow cubes, m. p. 114—115°, by coupling with diazotised *o*-toluidine; and a brownish-yellow *eurhodine*, m. p.



177—178°, of the formula (II), by condensation with *p*-nitroso-dimethylaniline.  
J. C. W.

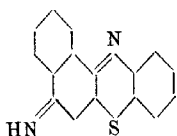
**2-Nitro-4-cyanobenzaldehyde and 6:6'-Dicyanoindigotin.**  
S. REICH and E. LENZ (*Helv. Chim. Acta*, 1920, **3**, 144—151).—2-Nitro-*p*-toluonitrile, colourless, shining needles, m. p. 107°, is prepared from 2-nitro-*p*-toluidine by a modification of the method of Niementowski and Noyes, and is converted by *p*-nitrosodimethylaniline in alcoholic solution in the presence of sodium carbonate into *p*-dimethylaminophenyl-2-nitro-4-cyanophenylazomethine [2-nitro-4-cyanobenzylidene-*p*-phenylenedimethyldiamine].

$\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_3(\text{CN})(\text{NO}_2)$ , almost black needles, m. p. 182.5—183° (decomp.), which is hydrolysed by hydrochloric acid, yielding 2-nitro-4-cyanobenzaldehyde, red needles, m. p. 110°. The latter yields an *oxime*, red needles, m. p. 142—143°, and a *phenylhydrazone*, bright red crystals, m. p. 202—203° (decomp.), which could not be converted by potassium hydroxide in aqueous-alcoholic solution into an *isoidazole* derivative, a fact which is interpreted as further evidence in favour of Reich's views on the influence of the accumulation of atoms and atomic groups round the aldehydic carbon atom on such condensations (compare Reich and Nicolaeva, A., 1919, i, 171). The aldehyde, when dissolved in benzene, is converted by exposure to sunlight into 2-nitroso-4-cyanobenzoic acid, small, yellow crystals, which begin to darken at about 210°, and have m. p. 250° (decomp.). When a solution of the aldehyde in acetone is treated with dilute sodium hydroxide solution, 6:6'-dicyanoindigotin is deposited as a bluish-violet powder with metallic lustre; when heated, it does not sublime, but decomposes, with evolution of reddish-violet vapours. When reduced with sodium hyposulphite, it dyes wool and cotton from an alkaline bath in reddish-purple shades, which become blue with a tinge of violet on exposure to air, oxidation proceeding more slowly than with indigotin. The shades are fast to light and milling.  
H. W.

**Preparation of Easily Soluble Compounds of the CC-Di-alkyl-, CC-Diallyl-, and CC-Alkylaryl-barbituric Acids.** F. HOFFMANN, LA ROCHE & Co. (Brit. Pat. 122778).—Easily soluble compounds of these acids are obtained by combining them with alkylamines, for example, diethylamine or dimethylamine, by add-

ing rather more than the theoretical amount of alkylamine to the free acid, so that the latter is dissolved, and then evaporating off the excess of amine. The products are more powerful hypnotics than the free acids, and much more stable in aqueous solution than their sodium salts.

**Action of *o*-Aminothiophenol on Orthoquinones. I. 5-Imino-7:12-naphthaphenthiazine.** KNUT STAHRPOSS (*Helv. Chim. Acta*, 1920, **3**, 134—138).—*o*-Aminothiophenol hydrochloride reacts with 4-amino-1:2-naphthaquinone in boiling 80% acetic acid

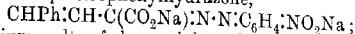


solution, with formation of 5-imino-7:12-naphthaphenthiazine hydrochloride, a chocolate-brown powder, which is stable in air and readily soluble in water. The *platinichloride* was analysed. The free base (annexed formula) is an unstable, yellow substance. The constitution of the substance follows from the conversion of the hydrochloride by concentrated sulphuric acid into a naphthaphenazthione, identical with that formed from *o*-aminothiophenol and 4-hydroxynaphthaquinone.  
H. W.

**New Bases for the Preparation of Mordant Dyes.** HEINRICH BAMBERGER (*Zeitsch. angew. Chem.*, 1920, **33**, i. 8).—The chlorides of *o*-nitrophenol-*p*-sulphonic acid, 6-nitro-*o*-cresol-*p*-sulphonic acid, and 6-nitrosalicyl-*p*-sulphonic acid, obtained by treatment of their potassium salts with chlorosulphonic acid, react quantitatively with aromatic amines, diamines, amino-carboxylic acids, or amino-phenols, and with amino-sulphonic acids or amino-phenolsulphonic acids of the benzene or naphthalene series. By reducing the resulting sulphamido-compounds with sodium sulphide, valuable bases are produced for mono- and bisazo-mordant dyes, which give colours ranging from yellow to bluish-violet (compare Swiss Pat. 81249—81256; Fr. Pat. 490177 [1918]).  
J. K.

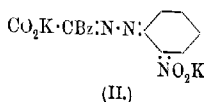
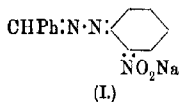
**Certain Salts with para-, ortho-, and meta-Quinonoid Structure.** R. CIUSA (*Atti R. Accad. Lincei*, 1919, [v], 28, ii, 366—371).—In contact with alkali, best in acetone solution, *p*-nitrophenylhydrazones are turned violet, addition of water to the solution or acidification yielding the initial hydrazones unchanged. That the corresponding salts, which are easily obtainable, differ in structure from the nitrohydrazones themselves is shown by their different colour in solution and by their different absorption spectrum. To explain the intense colour of these salts, the simple quinonoid constitution is insufficient, the assumption of the more complex formula,  $C_6H_4 \begin{smallmatrix} \text{NO}_2 \text{M} \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{CHPh}$ , in which the metal, M, is united by secondary valencies to the rest of the molecule, being necessary; the position at which the secondary valencies act is still uncertain. Similar complex formulæ are attributed to all the

quinonoid salts dealt with in the paper. The following salts have been prepared: the potassium salt of benzaldehyde-*p*-nitrophenylhydrazone,  $\text{CHPh}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\text{K}$ ; the disodium salt of benzylidenepyruvic acid-*p*-nitrophenylhydrazone,



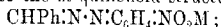
the dipotassium salt of benzoylglyoxylic acid-*p*-nitrophenylhydrazone,  $\text{CO}_2\text{K}\cdot\text{CBz}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\text{K}$ .

In alcoholic or acetone solution, *o*-nitrophenylhydrazones also dissolve in alkali, the solutions assuming a blue coloration. Crystalline salts of benzaldehyde-*o*-nitrophenylhydrazone have not been obtained, although the sodium salt (I) certainly exists in solution,



but the dipotassium salt of benzoylglyoxylic acid-*o*-nitrophenylhydrazone (II) has been prepared in shining, bronze-coloured crystals or as a blue powder.

It has been stated that benzophenone-*m*-nitrophenylhydrazone does not undergo salt formation in contact with alcoholic potassium hydroxide. The author finds, however, that a very slight change of colour does take place under these conditions, and that, in acetone solution, *m*-nitrophenylhydrazones give a green coloration with the alcoholic alkali, addition of water then resulting in the formation of the unaltered nitrophenylhydrazones. The absorption spectrum of such an alkaline solution differs from that of the original hydrazone, and persists even on dilution of the liquid. In this case, it has not been found possible to obtain crystallised salts, but it may be assumed that the salt formation occurs with change from the benzenoid to the *m*-quinonoid structure,



such *m*-quinonoid saline compounds are certainly readily hydrolysable, and the tendency to their formation small.

The experimental results are to be published elsewhere.

T. H. P.

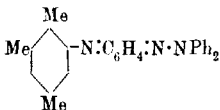
## Amine-oxidation. II. Bivalent Nitrogen. Triphenylhydra-*zyl*.

STEFAN GOLDSCHMIDT (*Ber.*, 1920, 53, [B], 44—62).—When an ethereal solution of triphenylhydrazine (Wieland, A., 1915, i, 797) is shaken with lead peroxide, a fugitive, deep blue solution is formed which has the characteristics of solutions of compounds with bivalent nitrogen (Wieland, *Ibid.*, 848). This suggests that oxidation to *hexaphenyltetrazane* has taken place, this being dissociated in solution into *triphenylhydra-*zyl**, thus:  $2\text{NPh}_2\cdot\text{NHPh} \rightarrow \text{NPh}_2\cdot\text{NPh}\cdot\text{NPh}\cdot\text{NPh}_2 \rightarrow 2\text{NPh}_2\cdot\text{NPh}$ ..... By carrying out the oxidation in methyl ether at  $-55^\circ$  to  $-60^\circ$ , the tetra-*zane* may actually be isolated as a very pale green crust, which is sparingly soluble in chilled ether or light petroleum, but more soluble in toluene or chloroform. The solutions are deep blue and

do not obey Beer's dilution law, thus confirming the idea\* of dissociation. The dissociation depends on temperature and on the solvent. For example, ethereal solutions, which are only pale greenish-blue at  $-80^{\circ}$ , are deep blue at the ordinary temperature, and chloroform solutions are darker than ethereal solutions under the same conditions. The substance may be analysed by means of quinol, this causing reduction to triphenylhydrazine, when the liberated quinone can be titrated iodometrically.

Triphenylhydrazyl is not sensitive to oxygen, but combines with nitric oxide at low temperatures to form *N*-nitrosotriphenylhydrazine, golden prisms, m. p.  $115^{\circ}$  (Busch, A., 1907, i, 552). It also combines with triphenylmethyl, but this agent reacts too slowly to permit of the isolation of a pure product before the triphenylhydrazyl has decomposed. The decomposition of triphenylhydrazyl is accompanied by change of colour, through green to reddish-brown, the products being diphenylamine and quinoneanildiphenylhydrazone,  $\text{NPh}_2\cdot\text{N}:\text{C}_6\text{H}_4:\text{NPh}$  (Wieland, A., 1911, i, 82). Ethereal solutions of triphenylhydrazine also develop the blue colour of triphenylhydrazyl on exposure to sunlight, and then yield the same decomposition products.

When a mixture of aniline and triphenylhydrazine in ether is oxidised by lead peroxide, benzoquinoneanildiphenylhydrazone is again formed. This is interpreted as the fusion of the two radicles,  $\text{NPh}_2\cdot\text{NPh} + \cdot\text{NPh} \rightarrow \text{NPh}_2\cdot\text{N}:\text{C}_6\text{H}_4:\text{NPh}$  (compare this vol., i, 226), and is confirmed by the fact that a mixture of cumidine and triphenylhydrazine gives a homologous compound (annexed formula), which crystallises in the form of its *hydrochloride* in bluish-violet, stout spikes, m. p.  $152-153^{\circ}$ . Both compounds exhibit only one absorption band, the aniline derivative at  $465-650\mu$  and the new one at  $475-525\mu$ . The identity of the new



compound is established by reduction to diphenylamine and *p*-aminophenylcumylamine,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_5\text{Me}_2$ , concentric groups of needles, m. p.  $86-87^{\circ}$ .

These facts are discussed in connexion with Wieland's views on the decomposition of triphenylhydrazine. It is suggested that the products are best interpreted by assuming an initial dissociation into H and  $\text{NPh}_2\cdot\text{NPh}\cdot$ .

When triphenylhydrazine is treated with ethereal hydrogen chloride at  $-20^{\circ}$ , it yields *N*-phenylbenzidine (Busch, *loc. cit.*). This is oxidised by lead peroxide in ether to *diphenoquinonephenyldi-imine*,  $\text{NPh}:\text{C}_6\text{H}_4:\text{C}_6\text{H}_4:\text{NH}$ , yellowish-red needles, m. p.  $180-181^{\circ}$ .

J. C. W.

**Hæmoglobin. I. Optical Constants.** WILLIAM H. WELKER and CHARLES SPENCER WILLIAMSON (*J. Biol. Chem.*, 1920, **41**, 75-79).—By employing the method of Marshall and Welker (*A.*, 1913, ii, 568) for removing small amounts of other colloids from

hæmoglobin solutions, the authors were able to prepare purer specimens of crystallised hæmoglobin, which could be used for the study of the absorption coefficients of the pigment from various species. The results obtained indicate that there is not sufficient difference in the absorption coefficients of the hæmoglobin of various species to serve as a means of identification of the species. J. C. D.

**The Structure of Yeast-nucleic Acid. V. Ammonia Hydrolysis.** P. A. LEVENE (*J. Biol. Chem.*, 1920, **41**, 19—23).—

The fourth nucleotide, *cytidinephosphoric acid*,  $C_9H_{14}O_8N_3P$ , m. p.  $225^\circ$  (corr.; decomp.),  $[\alpha]_D^{20} + 40$ — $43^\circ$ , has now been obtained in a crystalline condition. There is a danger of error in assuming the existence of di- or tri-nucleotides on the basis of the results of elementary analysis, for it is shown that the free nucleotides, as well as their brucine salts, are capable of forming mixed crystals, which may furnish analytical data very nearly approaching those required by polynucleotides. J. C. D.

**Crystalline Uridinephosphoric Acid.** P. A. LEVENE (*J. Biol. Chem.*, 1920, **41**, 1—2).—The crystalline diammonium salt of uridinephosphoric acid was converted into the lead salt, which was decomposed by hydrogen sulphide. From the concentrated filtrate, the free uridinephosphoric acid,  $C_9H_{13}O_8N_2P$ , was obtained in a crystalline condition, m. p.  $202^\circ$  (corr.; decomp.),  $[\alpha]_D^{20} + 10.5^\circ$ . This research marks an important step in the chemistry of yeast-nucleic acid, as every one of the four constituent nucleotides has now been prepared in crystalline form. J. C. D.

## Physiological Chemistry.

**Estimation of the Alkalinity of Blood.** PEDRO J. PANDO (*Rev. Farm., Buenos-Ayres*, 1919, 167; from *J. Pharm. Chim.*, 1919, [vii], **20**, 394—395).—A small flask containing 20 c.c. of water, 1 gram of 10% sodium citrate solution, and 10 c.c. of *N*/200-sulphuric acid is weighed; about 0.2 gram of blood is collected directly in the flask, which is again weighed. After the addition of 1 gram of animal charcoal, the mixture is diluted to 50 c.c., filtered, and 45 c.c. of the filtrate are titrated with *N*/200-sodium hydroxide solution, using phenolphthalein as indicator. By this method, normal blood exhibits an alkalinity equivalent to 5.50 grams of sodium hydroxide per 1000 grams. W. P. S.

**The Presence of Hæmatin in Human Blood Serum. III. Further Results from Toxicological Practice.** JOH. FRIGL (*Biochem. Zeitsch.*, 1919, **93**, 119—127. Compare A., 1918, i, 241).—From observations made on munition workers, it was found that



hæmatinæmia is an important phenomenon in the course of the decomposition of blood brought about by the toxic effect of nitrous fumes ( $\text{NO}_2, \text{N}_2\text{O}_3$ ), and is more apparent than the contemporary incipient methæmoglobinæmia. Out of about thirty cases of gas poisoning (from the front), eight showed hæmatinæmia ten to twenty-eight days after the intoxication. No definite information as to the presence of hæmatin in the serum of "Röntgen gas" cases is so far available. Hæmatinæmia was absent in cases of zinc, copper, and lead poisoning. A case of arsenic hydride poisoning showed hæmatinæmia. The histories of some of the cases are given.

S. S. Z.

**Antigens. XIII. The Significance of the Protein Components in the Precipitin Reaction of the Azoproteins.**

KARL LANDSTEINER (*Biochem. Zeitsch.*, 1919, **93**, 106—119. Compare A., 1918, i, 321).—Immune sera were prepared by the injection of azotised horse sera, prepared by the coupling of the serum with the diazo-compounds of aniline-*m*-sulphonic acid and *p*-arsanilic acid respectively. The precipitin reactions of the sera were then tested on various proteins azotised by means of the diazo-compounds of aniline-*m*-sulphonic acid and *p*-arsanilic acid. With the exception of gelatin and peptone, the aniline-*m*-sulphonic acid immune serum precipitated all the proteins azotised by means of the aniline-*m*-sulphonic diazo-derivative, but not the proteins azotised with the *p*-arsanilic acid derivative. The reverse happened with *p*-arsanilic acid immune serum. The author suggests that the usual immunological serum reactions do not depend on the specific chemical structure of the respective proteins, but on the dimensions of the molecule of these proteins.

S. S. Z.

**Availability of Carbohydrate in certain Vegetables.**

W. H. OLMSTED (*J. Biol. Chem.*, 1920, **41**, 45—58).—Vegetables of low carbohydrate content, such as cabbage, spinach, and lettuce, are frequently employed in the diet of patients with diabetes. Estimations of the sugar-forming material in such vegetables were therefore made, either by hydrolysis of the starch with diastase, followed by estimation of the dextrose by reduction of copper solutions, or by ascertaining the extra sugar excreted by a phloridzinised dog after administration of a known amount of the vegetable. The amounts of available carbohydrate in cabbage and cauliflower, as measured by the latter method, are of the same order as those recorded in the analyses of Atwater and Bryant. The "thrice cooking" process frequently employed to remove carbohydrates from vegetables intended for consumption by diabetic patients is effective in reducing the amount of carbohydrate present by 90%.

J. C. D.

**The Influence of Alkaline and Acid Hydrolysis on the Absorption and Utilisation of Proteins. I. The Utilisation of Hydrolysed Casein.**

JOHANNES MÜLLER and HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1919, **93**, 34—44).—Various

hydrolysis preparations of casein were fed to a terrier, and the nitrogen metabolism was worked out in order to ascertain the amount of the protein utilised by the animal. 96.1% of the original casein was retained by the dog. The same casein, hydrolysed by shaking with 3% sodium hydroxide and heating it for one and a-quarter hours in a boiling water bath under a reflux condenser, was only utilised to the extent of 59%. When the casein was heated with 3% sodium hydroxide for two hours under a pressure of four atmospheres, 39% of the hydrolysed product was retained. The administration of opium per os to the dog fed on the alkaline product of hydrolysis of casein did not improve its retention in the organism. On the other hand, 98.6% of the casein, hydrolysed by heating it with 2.74% hydrochloric acid in a boiling water bath under a reflux condenser for four hours, was utilised. Protalbic acid, prepared by hydrolysing casein with 3% sodium hydroxide under a reflux condenser and precipitating with acetic acid, was also tried. 29% of this product was retained.

S. S. Z.

**The Utilisation of Yeast in the Animal Organism.** W. VÖLTZ (*Biochem. Zeitsch.*, 1919, **93**, 101—106. Compare Schill, A., 1918, i, 359).—Living yeast, after a sojourn of six and a-half hours in the digestive tract of a dog, was excreted in the faeces in a living condition, and was capable of fermenting sugar. After remaining for nine and a-half hours inside the dog, the yeast cells were mostly dead, and about half of them were digested. The faeces in this case contained 5% of living, 20% of diseased, and 75% of dead cells. 53.3% of the total organic matter and 46.6% of the protein of the consumed yeast were utilised by the organism. It is therefore advisable to kill the yeast before utilising it for feeding purposes unless it is administered with a therapeutic object.

S. S. Z.

**Occurrence of Squalene in the Egg Oil of a Shark.** MITSUMARU TSUJIMOTO (*J. Ind. Eng. Chem.*, 1920, **12**, 73).—The oil separated from the eggs of the Japanese shark, *Lepidorhynchus kinbei* (Tanaka), by extraction with ether was a light brown, semi-solid substance with an iodine value of 177.6. When treated with dry hydrogen chloride, it yielded 20% of squalene hexahydrochloride. Squalene has also been found in the egg oil of the frill shark, *Chlamydoselachus anguineus* (Garman). [See, further, *J. Soc. Chem. Ind.*, 1920, 197A.]

C. A. M.

**Squalene: a Highly Unsaturated Hydrocarbon in Shark-liver Oil.** MITSUMARU TSUJIMOTO (*J. Ind. Eng. Chem.*, 1920, **12**, 63—72).—Of the numerous species of Japanese sharks, those having liver oils of low sp. gr. (below 0.9) usually have the hydrocarbon, squalene, in the oil (A., 1918, i, 89). This constituent may be approximately estimated by distilling the oil under reduced pressure in a current of carbon dioxide or other inert gas. The amount thus estimated in the liver oils of twelve species of sharks ranged

from 7.1 to 84.8%. Squalene isolated from the liver oil of the *Ai-zamé* shark had  $D_4^{25}$  0.8591 and  $D_4^{20}$  0.8559. Exposed to the air in a thin layer, it absorbed 13.4% of oxygen in three days and 24.0% in twenty-three days, the oxygen absorption, calculated from the formula  $C_{30}H_{50}O_6$ , being 23.66%. The dodecaboride,  $C_{30}H_{50}Br_{12}$ , when reduced with glacial acetic acid and zinc dust, yielded about 35% of an orange-yellow oil with  $n_D^{20}$  1.4950. The hexahydrochloride, when recrystallised from acetone, melted at about 125°. Its formation is the best test for the detection of as little as 1% of squalene in an oil. The hexahydrobromide forms white, lustrous crystals, turning brown at 115–118°, and melting at 125–126°, whilst the *hexahydriodide* is an unstable, white, crystalline compound, melting to a pink liquid at 108–109°. On dechlorinating the hexahydrochloride, a nearly colourless, oily liquid of  $D_4^{25}$  0.9065 was obtained. When distilled under reduced pressure, this yielded an oily distillate with iodine value 281, which appeared to be a hydroxy-derivative of squalene with the formula  $C_{30}H_{50}(OH)_2$ . It boiled at 252–254° (4.5 mm.), and had  $D_4^{25}$  0.8995 and  $n_D^{20}$  1.4938. Squalene yielded a yellow formolite, which decomposed at about 180°, but no crystalline nitrosochloride or nitrosite. On dry distillation, it yielded a small fraction, which was a hydrocarbon with molecular weight 131. Although squalene differs slightly in physical properties from the hydrocarbon, spinacene, isolated by Chapman from the liver oils of Portuguese sharks (T., 1917, 111, 56; 1918, 113, 458), it seems probable, from the similarity of the derivatives, that the two hydrocarbons are identical. [See, further, *J. Soc. Chem. Ind.*, 1920, 197A.]

C. A. M.

**Physiology of Glands. XXXVIII. The Influence of the Spleen on the Respiratory Metabolism.** NIKOLA DANOFF (*Biochem. Zeitsch.*, 1919, 93, 44–66).—The respiratory metabolism of rats was studied by means of Haldane's method. It was found that the respiratory metabolism of small animals is higher per unit body weight and time than that of larger animals, and that it rose as the surrounding temperature sank. Rats which had their spleen removed used up more oxygen and produced correspondingly more carbon dioxide than normal rats. These quantities rose from day to day soon after the operation. The respiratory quotient, however, remained the same before and after the operation. The presence of the spleen therefore reduces the respiratory metabolism, and its function in this respect is consequently opposite to that of the thyroid.

S. S. Z.

**Formation of Lactose in the Mammary Gland.** F. RÖHMANN (*Biochem. Zeitsch.*, 1919, 93, 237–253).—On digesting the extract of the mammary gland, dextrose was formed. This sugar was then converted into levulose and galactose, and eventually into lactose. These reactions were followed up by estimating the reduction, the rotation, the formation of mucic acid by oxida-

tion with nitric acid, and the osazone formation. The degree of the dextrose formation and its transformation into the other sugars in the extract of the mammary gland are found to be influenced by the condition of the activity of the gland at the time of the animal's death. Sucrose, which was added to the extract, was also degraded by it, and the products of degradation underwent further transformation. The formation of dextrose in the extract could not be of the character of a glucoside hydrolysis, as on heating the extract with 2—10% sulphuric acid, the reduction was only increased to a small extent. This increase in reduction was shown to be due to the splitting of small quantities of lactose. The author advances the hypothesis that dextrose, which reaches the mammary gland through the blood stream, is not always utilised immediately, but is sometimes stored there as an intermediate substance, which by some still unknown fermentation process can be reconverted into dextrose. The latter, by further enzymic activity, is converted into levulose and galactose, and eventually into lactose. S. S. Z.

**The Normal Arsenic of Living Tissues and the Traces of Iodine found in the Air and in Waters. Some Necessary Corrections.** A. GAUTIER (*Compt. rend.*, 1920, 170, 261—262).

—The author reaffirms the conclusions drawn from his previous work (compare A., 1900, ii, 152, 168, 226, 670; 1903, ii, 92) as to the occurrence of arsenic in animal tissues, but draws attention to possible errors in the estimation of arsenic, due to the presence of traces of hydrogen arsenide as an impurity in the hydrogen sulphide used.

Examination of further samples of sea-water from different sources, previously found to give water containing iodine in a soluble form, now shows the complete absence of iodine in a soluble form, although minute traces of it in an insoluble form were found.

W. G.

**Carbonic Acid and Carbonates in Cows' Milk.** LUCIUS L. VAN SLYKE and JOHN C. BAKER (*J. Biol. Chem.*, 1919, 40, 335—344).

—Considerable care must be taken over the collection of the sample to ensure that there is no loss of carbon dioxide. The analysis is carried out by the method previously described for the estimation of carbon dioxide in blood plasma (Van Slyke, A., 1917, ii, 422), with one or two slight modifications, the chief of which is the employment of a 20% solution of lactic acid to disengage the carbon dioxide. With the decrease in the hydrogen-ion concentration there is a general tendency for the carbon dioxide content of milk to increase and for the degree of acidity, as measured by titration, to decrease. The results are higher than those recorded by other workers, the normal content of carbon dioxide in milk being about 10% by volume. The carbon dioxide of milk may be completely removed by exhaustion, provided the milk is spread out in a thin film and kept in motion. The removal of carbon dioxide results in a decrease in the hydrogen-ion concentration. When

milk is pasteurised, the carbon dioxide content is decreased, but the hydrogen-ion concentration is unchanged. When the carbon dioxide has been completely removed prior to pasteurisation, the hydrogen-ion concentration increases appreciably. It is suggested that the decrease of carbon dioxide in pasteurised milk might be made the basis of a method for distinguishing pasteurised from normal milk.

Carbon dioxide in milk is present as carbonic acid and as bicarbonate, probably of sodium, the ratio being about 1 to 2. The tension of carbon dioxide in milk is calculated to be about 50—55 mm. of mercury at 20° in the case of a 0.01*N*-solution with  $p_H$  value of 6.60.

J. C. D.

**The Influence of the Acidity of the Milk on the Velocity of Inactivation of the Peroxydase by Heat.** A. BOUMA and W. VAN DAM (*Biochem. Zeitsch.*, 1918, **92**, 385—397).—The influence of the hydrogen-ion concentration on the inactivation of the peroxydase in milk at 70–55° was studied. At 70°, the  $p_H$  is two and a-half to three times higher than at the ordinary temperature. The addition of so much lactic acid to the milk as was just insufficient to curdle it on pasteurisation had no effect on the velocity constant of the inactivation of the enzyme at that temperature. On the other hand, the addition of sodium hydroxide and ammonia greatly accelerated the destruction of the peroxydase. This confirms the preliminary observations previously made by Zilva.

S. S. Z.

**The Physiological Action of the Proteinogenic Amines.**  
**I. The Influence of Proteinogenic Amines on the Nitrogen Metabolism of Dogs from which the Thyroid has been Removed.** J. ABELIN (*Biochem. Zeitsch.*, 1919, **93**, 128—149).—Phenylethylamine, *p*-hydroxyphenylethylamine, and eventually isoamylamine were administered per os to dogs from which the thyroid had previously been removed. An increase in the metabolism and greater diuresis were observed as a result of the treatment. A decrease in body weight was also recorded. As the pharmacological action of the above amines resembles that of the protein substances from the thyroid, it is suggested that the action of the thyroid on the metabolism is not due to the protein substances themselves, but to derivatives emanating from them.

S. S. Z.

**Physiological Action of Aromatic Diamines.** RICHARD MEISSNER (*Biochem. Zeitsch.*, 1919, **93**, 149—163).—*o*- and *m*-Phenylenediamines, in contradistinction to *p*-phenylenediamine, are tolerated by frogs in high doses. *o*-Phenylenediamine has also no toxic effect on rabbits. Cats, on the other hand, develop oedema typical of *p*-phenylenediamine intoxication on administration of the ortho-compound. *m*-Phenylenediamine produces no oedema in cats and rabbits, but the latter animal develops ascites. The methyl

derivatives of the above isomerides produce cerebral manifestations, and prove fatal even when given in small doses, but no œdema can be observed. The diethyl and monoacetyl derivatives, on the other hand, cause swellings in the head and neck. The insoluble diacetyl- and ethoxy-*p*-phenylenediamine are inactive. Triamino-benzene, -toluene, and -phenol produced methæmoglobinuria in cats, but not œdema.

S. S. Z.

**The Pharmacology of Compounds Resembling Digitalis in their Activity.** MARGARETE WALTER (*Biochem. Zeitsch.*, 1918, **92**, 267—282).—The diffusibility, electrical charge, adsorption, and the reversibility of the action on the heart of compounds resembling digitalis in their activity were studied. No connexion between these properties could be established.

S. S. Z.

## Chemistry of Vegetable Physiology and Agriculture.

**The Effect of Nitrogen-fixing Organisms and Nucleic Acid Derivatives on Plant Growth.** W. B. BOTTOMLEY (*Proc. Roy. Soc.*, 1920, [*B*], **91**, 83—95).—The crude nucleic acid derivatives from bacterised peat and the growth products from *Azotobacter chroococcum* or from *Bacillus radiclecola* each exert a very marked influence in increasing the growth of plants of *Lemna minor* in water culture. Not only is there an increase in the number of plants formed, but also in the weight of the plants. The crude nucleic acid derivatives, which are about as effective as the *Azotobacter* growth, are much more effective than the pure adenine-uracil dinucleotide derived from them. The joint effect of the crude nucleic acid derivatives and *Azotobacter* growth is much greater than the sum of their individual effects, being about equal to that of the water extract of an equivalent amount of bacterised peat. It is of interest to note that the crude nucleic acid derivatives, and the *Azotobacter* and *B. radiclecola* growths, all give the Folin-Macullum reactions, which are stated to indicate the presence of vitamins.

W. G.

**The Oxidation of Vanillin to Vanillic Acid by certain Soil Bacteria.** WILLIAM J. ROBBINS and E. C. LATHROP (*Soil Sci.*, 1919, **7**, 475—485).—In solution cultures containing mineral nutrients and vanillin, the latter being the only source of carbon, and inoculated with a bacterium present in certain Alabama soils, the vanillin was first oxidised to vanillic acid, which could be isolated, but was subsequently destroyed if left in the solution. Estes's reagent, acid mercuric nitrate, gives satisfactory results in the estimation of vanillin in the presence of vanillic acid (compare A., 1917,

ii, 343), but the phenol reagent of Folin and Denis (compare A., 1912, ii, 1011) is unsatisfactory under such conditions, as vanillic acid, like vanillin, gives a blue colour with this reagent, the colour produced by the acid being much deeper than that produced by an equivalent amount of the aldehyde. The authors find that vanillic acid has m. p.  $210.5-211^{\circ}$  (corr.). W. G.

**Chemical Enzyme Studies. The Growth of Yeast in Alkaline Solutions.** HANS VON EULER and OLOF SVANBERG (*Arkiv Kem. Min. Geol.*, 1918, 7, No. 11, 1-13).—The maximum alkalinity of the medium in which a Froberg bottom yeast grew was between  $P_H=7.7$  and  $P_H=8$ . A distillery top yeast (SB II) showed decided growth at  $P_H=7.3$ . The maximum, however, tolerated by growing yeast depends to a great extent on the quantity of cells seeded. The maximum alkalinity for *Saccharomyces ellipsoideus* and *Pseudosaccharomyces apiculatus* was  $P_H=7.9$  and  $P_H=7.6$  respectively. The highest limit of alkalinity tolerated by *Aspergillus niger* was found to be  $P_H=9$ . S. S. Z.

**The Presence of Non-volatile Substances Possessing Aldehydic Properties in Yeast Macerations.** J. COCHIN and R. SAZERAC (*Bull. Soc. chim. Biol.*, 1914, 1, 75-77).—The authors have observed that the maceration fluids from pressed yeast give a reddish-violet colour with Schiff's reagent. The substances which give this reaction are not volatile, so that they cannot be identified with the lower aldehydes. Their exact nature has not yet been determined. J. C. D.

**Presence and Estimation of Tryptophan in Protein Material of Yeast.** PIERRE THOMAS (*Bull. Soc. chim. Biol.*, 1914, 1, 67-74).—The content of tryptophan in caseinogen is approximately 1.7 to 1.8%. The protein substance from yeast, *cérévisin*, contains about 2.3%, and is the substance containing the highest percentage of tryptophan which is known. It also contains a high percentage of lysine, a fact which places this protein in a class by itself. J. C. D.

**Invertase and Fermentation Enzymes in a Top Yeast.** HANS VON EULER and E. MOBERG (*Arkiv Kem. Min. Geol.*, 1918, 7, No. 12, 1-17).—The production and the activity of the invertase of a top yeast were only influenced to a small extent by a protoplasma poison, such as chloroform. In the top yeast investigated, it was not possible to augment the invertase by Euler's method to the extent previously done in bottom yeasts. It was further found from comparative experiments with fresh yeast that, after drying it, practically the entire invertase content was retained by the dried preparation. The amount of alcohol and carbon dioxide produced from a certain quantity of sugar in alkaline solution by dried and fresh yeast was approximately the same, and was not influenced by the addition of co-enzyme. The co-enzyme, previously heated with

sodium hydroxide, became, however, more active. The authors conclude that, besides the co-enzyme and phosphate, fermentation in alkaline solution requires another activator, most probably of the nature of an alkali salt.

S. S. Z.

**The Behaviour of certain Dyes towards Yeast-cells.**

HANS VON EULER and N. FLORELL (*Arkiv Kem. Min. Geol.*, 1919, 7, No. 18, 1—27).—Dyes are adsorbed by yeast in two ways. Some dyes penetrate the cell and are retained therein; others are adsorbed on the surface of the cell. In the former case, the cell shows the stain under the microscope; in the latter, the stain can only be detected in reflected light. The surface adsorption is the more common phenomenon of the two, and is greatly controlled by the previous preparation, especially washing, of the yeast. The adsorption in both cases is influenced by such factors as the concentration of the dye, temperature, hydrogen-ion concentration, and the presence of a fermentable sugar in the solution. The staining of yeast with chrysodine (diaminoazobenzene hydrochloride), janus-blue (safraninazo- $\beta$ -naphthol hydrochloride), ponceau 3R (sodium salt of cumidineazonaphtholdisulphonic acid), and methylene-blue impairs its fermenting capacity.

S. S. Z.

**The Culture of *Aspergillus niger* (Sterigmatocystis nigra, V. Tgh.) in Mediums in which Zinc is Replaced by Other Elements (Copper, Uranium, Vanadium).**

M. JAVILLIER (*Bull. Soc. chim. Biol.*, 1914, 1, 55—66).—*Aspergillus niger* requires, in addition to the elements carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, potassium, silicon, magnesium, iron, and manganese provided in suitable form, a trace of zinc. The author believes that the zinc plays the rôle of a physiological catalyst, and that it is not replaceable, in the strict sense of the word, by any of the elements examined.

J. C. D.

**The Aerial Fertilisation of Plants with Carbon Dioxide.**

M. B. CUMMINGS and C. H. JONES (*Bull.*, 1919, 211, 56 pp.).—A number of plants were grown in boxes and frames in the greenhouse, the boxes having glass covers, and a current of carbon dioxide was kept constantly flowing into the enclosure. With legumes, the carbon dioxide caused an increased production of pods and beans and slightly changed the chemical composition of the plant by increasing the carbohydrate storage. With peas, the increase of seed yield was especially marked. Radishes responded only slightly, but were marketable soon, and contained a larger carbohydrate and smaller protein content. Potatoes produced more foliage and larger and better tubers when grown in an atmosphere of carbon dioxide. The stimulating effect was very marked with strawberries, and the growth of flowers was also better. In most cases where the plants were grown with carbon dioxide, a higher carbohydrate content was found and a lower protein content. Lettuce was most benefited when given 300 litres of carbon dioxide per day in boxes 130 × 70 × 30 cm.

CHEMICAL ABSTRACTS.



**The Distribution of Glycerophosphatase in Seeds.** ANTON NĚMEC (*Biochem. Zeitsch.*, 1919, **93**, 94—101).—Oil-bearing seeds show a higher content of glycerophosphatase than do leguminous seeds. The latter, however, are richer in this enzyme than the cereals. S. S. Z.

**The Change in the Character of the Nitrogen in Germinating Lupines. The Relation of the Nitrogen Titratable with Formol and the "Formalin Nitrogen" to the Total Nitrogen.** H. SERTZ (*Biochem. Zeitsch.*, 1919, **93**, 253—255).—On the addition of neutral aqueous formaldehyde to plant albumins, albuminates, and hemialbumoses, the proteins become almost insoluble. This is referred to as "formalin nitrogen." The author has determined the relation of the nitrogen in the amino-groups which combines with formol and the "formalin nitrogen" to the total nitrogen in germinated lupines at various periods of the germination. The following are the results. Before germination: formol nitrogen=12.7%, "formalin nitrogen"=86.3%. After three days' germination: formol nitrogen=18.3%, "formalin nitrogen"=82.3%. After five days: formol nitrogen 24.9%, "formalin nitrogen" 70.5%. After seven days: formol nitrogen 31.05%, "formalin nitrogen" 65.5%. After ten days: formol nitrogen 39.4%, "formalin nitrogen" 57.6%. This demonstrates the formation of soluble amino-acids at the expense of the insoluble proteins during the germination of the lupine. S. S. Z.

**Germination and Formation of Chlorophyll in a Confined Atmosphere deprived of Carbon Dioxide.** N. A. BARBIERI (*Bull. Soc. chim.*, 1919, [iv], **25**, 658—661).—A comparative study of the germination of wheat in an atmosphere deprived of carbon dioxide, in pure oxygen, and in free air, in sunlight and in the dark. All germination or commencement of germination is marked by an elimination of carbon dioxide, with the formation of chlorophyll in sunlight and of chromophyll in the dark. In an atmosphere of pure hydrogen or nitrogen there is only a slight commencement of germination. In an atmosphere of pure carbon dioxide, germination does not take place. W. G.

**The Electrometric Titration of Plant Juices.** A. R. C. HAAS (*Soil Sci.*, 1919, **7**, 487—491).—The method used was that of the gas-chain, essentially of the form described by Hildebrand (*Univ. Cal. Pub. Physiol.*, 1919, **5**, 44—69), a simplified and inexpensive type of apparatus being described. Measurements were made on soja bean tops and rhubarb stalk, and from the curves, knowing the  $P_H$  values at which various indicators change colour, it is possible to tell the amount of standard alkali required to bring the plant juice to the turning point for any indicator. The curves given show the presence of greater quantities of buffer substances in the juice of the rhubarb than in the juice of soja bean tops, the actual acidity of the rhubarb juice being much greater than that of the juice of soja bean tops. W. G.

**Hydrogen-ion Concentration of Plant Juices. I. The Accurate Determination of the Hydrogen-ion Concentration of Plant Juices by means of the Hydrogen Electrode.**

CLINTON B. CLEVINGER (*Soil Sci.*, 1919, 8, 217—226).—In the method described, a Clark electrode vessel (compare A., 1916, ii, 75) modified and adapted for work with plant juices, a simple shaking apparatus, and calomel electrodes immersed in a constant temperature water-bath are used. The apparatus is so arranged that the plant juices are saturated with hydrogen outside the electrode vessel, and only come in contact with the electrodes just prior to the readings being taken. Contact between the plant juice and the saturated potassium chloride solution is made by means of a scratch around the cock connecting the two, thus reducing the contact potential, which develops quite rapidly when the connexion is made by opening the cock wide. Duplicate measurements usually agree within 0.1 millivolt, and constant potentials are maintained for several minutes. The plant juice is prepared by macerating the tissue, wrapping it in a muslin cloth, and expressing the juice by means of a press. This gives a juice free from coarse colloidal or other material.

W. G.

**Hydrogen-ion Concentration of Plant Juices. II. Factors Affecting the Acidity or Hydrogen-ion Concentration of Plant Juices.**

CLINTON B. CLEVINGER (*Soil Sci.*, 1919, 8, 227—242. Compare preceding abstract).—In making determinations of hydrogen-ion concentration of plant juices, certain points must be noted. Expressed plant juice usually becomes more acid on keeping, whilst plants when cut and left some time before the juice is expressed usually become more alkaline. Further, it is shown that the acidity of the leaves and stems is highest in the morning and decreases during the day, whereas the acidity of the roots is highest during the day. The decreased acidity of the leaves and stems in the day is attributed to the destruction of the accumulated acids by influences such as increased light and higher temperatures.

Oats, buckwheat, soja beans, and cowpeas were grown on acid soils and on the same soils after liming, and it was found that, with the exception of buckwheat, the tops of the plants grown on the limed soil were usually more acid than the tops of those grown on the unlimed soil. The acidity of the roots of the plants appeared to be comparable with that of the soil.

Similarly, the type of fertiliser used appears to have some influence on the acidity of plants. Thus, the acidity of the tops of oats grown on unlimed soil was less than that of those grown on limed soil when sodium nitrate or ammonium nitrate was used as a source of nitrogen.

W. G.

**A Method for the Macrochemical Examination of Substances contained in Cells.** FRITZ NETOLITZKY (*Biochem. Zeitsch.*, 1919, 93, 226—230).—When the finely ground powder of *Cortex quillajae* is shaken with chloroform, a sediment, con-

sisting mostly of crystals, is deposited at the bottom. These are crystals of calcium oxalate, and contain impurities such as sand grains and cell débris. The impurities can be removed by fractional sedimentation by shaking up the deposit with chloroform, carbon tetrachloride, or bromoform. The specific gravity of the latter can be altered by the addition of alcohol or ether. By this fractional method of differential sedimentation, a powder consisting almost of pure crystals was obtained. Such purified powder showed a content of 103.7% of CaO (calculated from the formula  $\text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$ ). By titrating the oxalic acid with permanganate, 94.8% of the theoretical amount was obtained. It is suggested that "sand" impurities were responsible for the high calcium and low oxalic acid content. From the above figures, the author also concludes that the crystals from *Cortex quillajae* have the formula  $\text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$ . The calcium oxalate thus obtained was further decomposed with sulphuric acid. The liberated oxalic acid, which was recrystallised several times, was titrated with permanganate, and 99.23% of the theoretical value was recorded. The crystals obtained both from sesame seeds and *Saponaria officinalis* by sedimentation from carbon tetrachloride were too contaminated with organic matter to yield good results, but the low calcium content of the sediment is most probably also due to the higher water of crystallisation of the crystals. By this method, it is also possible to separate other substances, like aleurone grains, calcified membranes, etc., from powdered plants. S. S. Z.

**Fixation of Calcium by Calciferous Plants.** (MILL) T. ROBERT (*Bull. Soc. chim. Biol.*, 1914, 1, 85-92).—Calciferous plants (les plantes calcifuges) are plants which possess a marked ability to absorb calcium. They are able to live in soil deficient in calcium by virtue of this increased power of assimilation. Another class (les végétaux calcicoles) are, on the contrary, possessed of a very low power of absorbing calcium. These require soils rich in calcium, and are able to live in the presence of an amount of calcium which would be toxic to plants of the former group. J. C. D.

**The Distribution and Migration of Copper in the Tissues of Green Plants.** L. MAQUENNE and E. DEMOUSTY (*Compt. rend.*, 1920, 170, 87-93).—Copper has been shown to be present in a large number of plants and trees and in all parts of the plants. It accumulates most in the parts of the plants where there is most water and great vital activity. The parts which gradually dry up and become old gradually lose their copper, yielding it to the growing parts. The copper is thus present in a diffusible and migratory form, its migration, except in so far as amount is concerned, being comparable with that of mineral nutrients, such as potassium. The juice of all the plant organs contains copper, sometimes in comparatively large amount, sometimes only in very small amount. W. G.

**Mode of Occurrence of Hydrogen Cyanide in Plants.**

L. ROSENTHALER (*Schweiz. Apoth. Zeit.*, 1919, 57, 571—576. Compare this vol., i, 130).—The author destroys disturbing enzymes by 2% silver nitrate, or, preferably, 5% mercuric chloride solution, which also fixes hydrogen cyanide if present as such. Mercuric cyanide is formed, and is dissolved by potassium iodide in slight excess; hydrogen cyanide is then liberated by carbon dioxide.

The mercuric chloride method differentiates only between hydrogen cyanide in glucosidal (for example, amygdalin) and non-glucosidal (loose) combination (for example,  $\text{Ph}\cdot\text{CO}_2\text{H}\cdot\text{HCN}$ ), but not between the latter and free hydrogen cyanide. The silver nitrate method might do so, since silver nitrate does not at once decompose the compound,  $\text{Ph}\cdot\text{CO}_2\text{H}\cdot\text{HCN}$ . Even boiling 5% mercuric chloride solution does not liberate hydrogen cyanide from amygdalin.

Hydrogen cyanide is stated to occur only combined as glucoside in bitter almonds, cherry, laurel leaves, linsced sprouts, peach leaves, *Sorghum vulgare* leaves, and the seeds of *Phaseolus lunatus*. The occurrence of hydrogen cyanide in non-glucosidal form in the buds of cherry laurel and the young leaves of *Sambucus niger* was proved by the mercuric chloride method. The leaves of *Panquium edule* and of *Alocasia macrorrhiza* probably also contain hydrogen cyanide in similar loose combination. The occurrence of free hydrogen cyanide in plants has not been observed. CHEMICAL ABSTRACTS.

**Distribution and Migration of Mineral Salts in an Annual Plant.**

G. ANDRÉ (*Bull. Soc. chim.*, 1919, [iv], 25, 610—613).—A study of the distribution of the ash and its components in the different parts of the tall sunflower (*Helianthus annuus*) at the stage of maturity. The roots and stem contain a very small proportion of the total ash, and what is present is poor in phosphates and sulphates and rich in potassium. The leaves contain practically one half of the total ash content of the plant. This portion of the ash is very rich in lime, and comparatively so in magnesia, but very poor in potassium. The capitule contains a low percentage of ash, which is rich in phosphates and potash. The seeds contain about one-tenth of the total ash of the plant, and this portion of the ash is extremely rich in phosphates. Of the nitrogen content of the plant, about one-half is to be found in the seeds, one-quarter in the leaves, and one-eighth in the capitule. It is only in the seeds that the ash contains a higher percentage of magnesia than of lime.

W. G.

**Constituents of the Leaves of *Helinus ovatus*.**

JOHN AUGUSTUS GOODSON (*T.*, 1920, 117, 140—144).

**The Inversion of Sucrose during the Preservation of Oranges.**

G. ANDRÉ (*Compt. rend.*, 1920, 170, 126—128).—The amount of sucrose undergoing inversion during four months in the half of an orange kept in presence of an antiseptic appar-

ently bears no relationship to the acidity of the orange expressed in terms of citric acid. Further, the actual inversion is much less than that occurring in an aqueous solution of sucrose, dextrose, and citric acid, and at about the same concentrations as in orange juice kept for seventy-eight days at the ordinary temperature. Accepting Marlinand's views as to the absence of sucrose in orange juice (compare A., 1907, ii, 644), the explanation offered is that the mixture of sucrose and citric acid is not homogeneous in the orange, the two substances being localised in different cells. W. G.

**The Inversion of Sucrose in Orange Juice.** G. ANDRÉ (*Compt. rend.*, 1920, 170, 292—295. Compare preceding abstract).—The hydrolysing action of the citric acid present in orange juice on the sucrose also present is very marked at the ordinary temperature. The action of the invertase present is also marked, but less intense than that of the citric acid. W. G.

**Properties of Plants of the Order Polygonaceæ.** A. J. STEENHAUER (*Pharm. Weekblad*, 1919, 56, 1084—1101).—The botanical structure of the leaves of many plants of the order *Polygonaceæ* is described. As regards their chemical components, no extensive research has so far been carried out, but various salts, ethereal oils, etc., have been identified in certain plants. The extraction of these from the leaves is described. Anthraquinone derivatives were found in *Polygonum convolvulus*, L., *P. dumetorum*, L., *P. sachalinense*, Schm., *P. Sieboldii*, Hort., and possibly *P. cilinode*, Michx. For the estimation of hydroxyanthraquinone derivatives, a colorimetric method is most suitable. W. J. W.

**The Flavones of Rhus.** CHAS. E. SANDO and H. H. BARTLETT (*Amer. J. Botany*, 1918, 5, 112—119).—By the isolation of flavone pigments from *Rhus typhina*, *R. glabra*, and *R. copallina*, the authors have been able to verify the conclusions of Perkin that the same flavone is not likely to be found in both the wood and leaves of the same species. Fisetin is distinctly a wood flavone, and appears to be an end-product of metabolism. It is now known to be present in *R. cotinus*, *R. rhodanthema*, *R. typhina*, and *R. glabra*. The first two species do not belong to *Rhus* in the restricted sense, but to the genera *Cotinus* and *Rhodospaera* respectively. The authors' studies are therefore the first to demonstrate the presence of fisetin in wood of species belonging to *Rhus* proper (the true sumacs). The distinctive leaf flavone, probably a plastic substance, of *Rhus* proper is myricetin. It has been obtained from *R. Coriaria*, and the authors have been able to detect it in *R. glabra* and *R. copallina*. The authors have not been able to trace its relationship to the fisetin of the stem or to the anthocyanins of the leaves and berries. Methods of extracting fisetin and myricetin are fully described. Colour reactions and physical properties of both flavones are given, together with analytical data for the acetyl derivatives and the purified flavones.

CHEMICAL ABSTRACTS.

**Colour Changes of Sugar-cane Juice and the Nature of Cane Tannin.** F. W. ZERRAN (*J. Ind. Eng. Chem.*, 1919, 11, 1034—1036).—The polyphenol present in sugar-cane juice, which gives a green coloration with ferric salts, and, together with oxydases and iron salts, is responsible for colour changes in the juice, is not catechol, but a true tannin derived therefrom. When heated alone, it produces catechol, but no pyrogallol; dilute acids give rise to a phlobaphen and protocathechuic acid, whilst fusion with potassium hydroxide yields protocathechuic and acetic acids, but neither gallic acid nor phloroglucinol.

J. H. L.

**Identification of Citric Acid in the Tomato.** R. E. KREMERS and J. A. HALL (*J. Biol. Chem.*, 1920, 41, 15—17).—The presence of citric acid in tomato juice has been confirmed by the isolation of its triphenacyl ester.

J. C. D.

**The Effect of Hydrogen Cyanide on Plants.** C. WEHMER (*Biochem. Zeitsch.*, 1918, 92, 364—376).—Green cress is killed within ten days by 0.24 mg. of hydrogen cyanide per 1 litre of air. In order to achieve the same effect with seeds placed in water, 71.3 mg. of the acid per litre of air are required, although 2.375 mg. of the poison per litre of air greatly impair their germination and development. Green leaves submerged in water are also killed by very dilute solutions of hydrocyanic acid.

S. S. Z.

**The Influence of Arsenious Acid on Growing Tissues.** RUDOLF COBET (*Biochem. Zeitsch.*, 1919, 98, 294—314).—The influence of arsenious acid on various plants and lower animals was studied. In the plants, no improvement in the growth was observed by the application of arsenious acid. Concentrations of 1/200,000 were found to be very toxic. Frogs' spawn and tadpoles were not so susceptible to the toxic effect of arsenious acid, but neither improvement nor retardation in growth of these organisms could be traced to the influence of the arsenic compound.

S. S. Z.

**Enzymes. I. Amylase of Germinated Barley.** D. MAESTRINI (*Atti R. Accad. Lincei*, 1919, [v], 28, ii, 393—394).—A highly active amylase solution may be obtained by extracting germinated barley with water containing 0.003 mol. % of acetic acid for at least six hours. [See, further, *J. Soc. Chem. Ind.*, 1920, March.]

T. H. P.

**Enzymes. II. Protease and Lipase of Germinated Barley.** D. MAESTRINI (*Atti R. Accad. Lincei*, 1919, [v], 28, ii, 456—458).—The protease and lipase of germinated barley are not extractable by water, being found, not in the filtrate, but only in the residual emulsion. If distilled water is used for the extraction, the emulsion shows no proteolytic, and but slight lipolytic, activity; if, however, the water contains 0.003 mol. % of acetic acid, the emulsion exhibits

both activities to a marked extent. [See, further, *J. Soc. Chem. Ind.*, 1920, March.] T. H. P.

**Fat-soluble Vitamine. III. The Comparative Nutritive Value of White and Yellow Maize.** H. STEENBOCK and P. W. BOUTWELL (with the co-operation of E. G. GROSS and MARIANA T. SELL (*J. Biol. Chem.*, 1920, **41**, 81—96).—The occurrence of yellow pigment and the growth-promoting property attributed to the presence of the fat-soluble vitamine seem to be intimately associated in the maize kernel. J. C. D.

**Activity of Soil Acids.** R. E. STEPHENSON (*Soil Sci.*, 1919, **8**, 41—59).—Using a modification of Tacke's method, previously described (*ibid.*, 1918, **6**, 33), an endeavour has been made to arrive at the degree of activity of the soil acids, the lime requirements being determined by allowing different times of contact for the soil and calcium carbonate. It is shown that the more reactive acids, which are capable of giving a toxic hydrogen-ion concentration, react rather quickly, but that some soils contain a large reserve of activity, which may be described as potential rather than active, but which is, however, capable of slowly decomposing carbonates. Rather highly buffered solutions react rapidly with calcium carbonate, even in the presence of soil, thus indicating that even the more active fractions of the soil acids may be considerably buffered. So far as tested, protein materials and amino-acids, previous to decomposition in the soil, do not react readily with carbonates. The author considers that the total potential acidity of a soil, as commonly determined, does not give sufficient information. It is necessary also to know something of the activity of the acids. It is not the capacity of a soil to decompose calcium carbonate, but rather the intensity of decomposition which is most highly significant.

In a discussion on the origin of soil acidity, the development of an acid condition in soils is considered from three points of view, namely, mineral acids, organic acids, and colloids. The weathering of rocks tends to give acid aluminosilicates and silicic acids, resulting in a comparatively large reserve of slowly reactive acids. Toxic acid reactions are, however, more probably due to the presence of more soluble and highly ionised acids, such as sulphuric, hydrochloric, or nitric acids, generally introduced by the application of fertilisers. It is only occasionally, and in highly organic, badly drained soils, that organic acids accumulate to a detrimental extent; in fact, in some soils organic matter may quite likely depress the more active acidity by buffering and by supplying a base in the form of ammonia and its derivatives. W. G.

**Hysteresis of Aqueous Solutions of Humus Earth.** HEINRICH FUCHNER (*Kolloid Zeitsch.*, 1919, **25**, 196—207).—An examination of peat shows that a clear, dark yellow solution may be obtained by digesting it with cold water. During the solution,

a faintly acid, somewhat aromatic odour is noticeable. The solution obtained has an acid reaction, and, on keeping for several days, deposits a slimy, brown substance, and the clear solution then becomes alkaline. The deposit from the solution obtained from 50 grams of peat amounts to 0.490 gram, and, on incinerating this, a residue of 0.218 gram is obtained. The ignited residue contained alumina, ferric oxide, manganese oxide, lime, magnesia and alkalis, sulphate, silicate, and phosphate. The solution and the deposit were examined microscopically immediately after preparation and after measured intervals, and it is shown that, after keeping for some time, changes occurred in them, notably the formation of crystals. The clear solution after sedimentation is shown to contain gels of alumina, ferric hydroxide, and silicic acid. Microphotographs of the various preparations are reproduced in the paper.

J. F. S.

**The Carbonation of Burnt Lime in Soils.** WALTER HOGE MACINTIRE (*Soil Sci.*, 1919, 7, 325—453).—A detailed study of the rate and manner of carbonation of calcium oxide and hydroxide, as such, or when mixed with soil under various conditions.

Dry calcium oxide or hydroxide does not react with dry carbon dioxide, but a very small amount of water suffices to start the action. The ignition of calcium hydroxide gives an oxide which, in small quantities, carbonates more rapidly when exposed to moist air than does the original hydroxide. The formation of carbonate from the hydroxide is controlled by the amount of free water available to convert the calcium hydroxide from solid to solution phase. The conversion of calcium oxide to the carbonate must be preceded by the formation of the hydroxide and its solution, but when moist carbon dioxide is present the two actions are so rapid as to be considered as simultaneous. The carbonation of calcium hydroxide in atmospheric exposure tends to be checked after a time by the formation of a protecting film-coating of carbonate round included nuclei of the hydroxide.

The general conclusions to be drawn from the extensive pot and field trials are as follows: Calcium oxide or hydroxide when applied at the rate of 2—4 tons per acre will revert to the carbonate more rapidly when left on the soil surface than when mixed with a dry mulch or the moist soil, the reversion being most rapid during humid atmospheric conditions. If a dressing of the oxide or hydroxide is left on the surface for several days prior to incorporation with the soil, the treatment is in effect equivalent to an application of finely divided calcium carbonate. If the oxide or hydroxide is incorporated with the top layer of soil, prior to a more thorough dissemination throughout the soil, the concentration may be sufficient to effect a temporary, partial sterilisation in this layer, which may have beneficial results. The first action of the calcium oxide applied to the soil is with the atmospheric and soil moisture, and there is no indication, when this is completed, of any tendency



to cause chemical disintegration of soil organic matter. Neither calcium oxide nor hydroxide, when applied in the amounts commonly used in practice, can be considered as chemically destructive of soil organic matter. [See, further, *J. Soc. Chem. Ind.*, 1920, 124A.] W. G.

**Calcium Cyanamide and Dicyanodiamide as Vegetation Factors.** EDUARD LINTER (*Inaug. Diss.*, 1917; from *Bied. Zentr.*, 1919, 48, 414—417).—In contact with sand or clay in presence of carbon dioxide, dicyanodiamide solution undergoes no change, but humous soils are able to absorb the dicyanodiamide with avidity, the poisonous effect on vegetation gradually disappearing. [See also *J. Soc. Chem. Ind.*, 1920, 166A.] T. H. P.

**Prevention of Volatilisation of Ammonia by means of Calcium Chloride.** A. STUTZER (*Fühling's Landw. Zeit.*, 1919, 68, 59—63).—Five grams of a sulphate or chloride of an alkali or alkaline earth metal were boiled for fifteen minutes with 250 c.c. of ammonium carbonate solution containing 0.25 gram of nitrogen; the percentage of ammonia which was volatilised was 77 with potassium, sodium, or calcium sulphate, 80 with magnesium sulphate, 87 with potassium chloride, 88 with sodium chloride, 83 with magnesium chloride, and 17 with calcium chloride. Five % of the ammonia volatilised from a solution of ammonium chloride which was exposed with calcium carbonate to the air for twelve days. The addition of 2 parts, 4 parts, and 6 parts of calcium chloride to 1 part of a volatile ammonium salt prevents 25, 50, and 75%, respectively, of the ammonia from volatilising; to preserve 90% or more of the ammonia, 8 parts of calcium chloride must be added for 1 part of nitrogen. Good results are secured when 6 parts of calcium chloride, which is a better conserving medium than gypsum, are added to urine for every 1 part of nitrogen.

#### CHEMICAL ABSTRACTS.

**Guano from Sardinia.** M. GIUA (*Gazzetta*, 1919, 49, ii, 246—249).—The author has analysed a number of samples of bat guano from the Borutta grotto at Sassari, Sardinia. Streaks or veins of a white, friable material, greasy to the touch, occur in the guano, particularly in that of recent origin; this consists of tri-calcium phosphate, together with calcium carbonate, silica, oxides of iron, aluminium and magnesium, and small proportions of nitrates, and resembles ordinary phosphorite, being formed by the action on the calcium carbonate of the surrounding rock either of the phosphoric acid present in freshly formed guano or of ammonium phosphate. The occurrence of this material in the guano is regarded as confirmation of the view that many phosphatic deposits owe their origin to deposits of guano. T. H. P.

## General and Physical Chemistry.

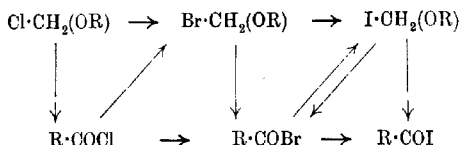
**The Optics of Disperse Systems. III.** I. LIFSCHITZ and GEORG BECK (*Kolloid Zeitsch.*, 1920, 26, 10—15. Compare A., 1918, ii, 181, 253).—The authors have measured the refractive index of solutions of triethylamine, gelatin, and phenol in water and of silicic acid, stannic acid, arsenic sulphide, antimony sulphide, and vanadium pentoxide sols in water by the method previously described (*loc. cit.*). The measurements were made at a series of temperatures with the object of ascertaining the effect of change in the dispersity on the refractive index. It is shown that the degree of dispersion is practically without effect on the refractive index. In the cases of phenol and triethylamine, where on lowering the temperature beyond the critical solution temperature a separation of the two liquids occurs, there is only a very small change of refractive index shown. In the case of gelatin the value of the specific refraction varies very much with the temperature, whether calculated by the Gladstone and Dale formula or by the Lorenz and Lorentz formula. In all other cases the value is approximately constant when either formula is used, but the values given by the Gladstone and Dale formula are more nearly constant than the others. J. F. S.

**The Spectrochemical Behaviour of Halogen Ethers, RO·(CH<sub>2</sub>)<sub>n</sub>·X, Halogen Hydrins, HO·(CH<sub>2</sub>)<sub>n</sub>·X, and Acid Bromides, R·COBr.** A. KÄRVOEN (*Acad. Sci. Fennicae*, 1914, A, 6, 1—139; from *Chem. Zentr.*, 1919, iii, 807—808).—In continuation of previous work (A., 1913, i, 2) a series of halogen ethers and halogen hydrins has been refractometrically investigated. New values for the atomic refraction of chlorine, bromine, iodine, and oxygen have been deduced from observations on normal primary alkyl monohaloids and the mono-ethers of normal primary alcohols. The data obtained for chlorine and iodine agree excellently with Eisenlohr's figures; on the other hand, the new values for bromine and ethereal oxygen differ considerably from the older results. The following figures are quoted:

	H <sub>a</sub> .	D.	H <sub>b</sub> .	H <sub>c</sub> .	H <sub>d</sub> - H <sub>e</sub> .	H <sub>f</sub> - H <sub>g</sub> .
Br-CH <sub>2</sub> - ..... 8·688	8·688	8·748	8·888	9·010	0·199	0·318
O $\begin{cases} \text{CH}_2- \\ \text{CH}_2- \end{cases}$ ..... 1·721	1·721	1·728	1·738	1·755	0·017	0·033

The α-halogen ethers, particularly the iodo- and bromo-derivatives, show optical exaltations in the order Cl·CH<sub>2</sub>(OR) < Br·CH<sub>2</sub>(OR) < I·CH<sub>2</sub>(OR), whilst the behaviour of the β- and γ-halogen ethers and of the β- and γ-halogenhydrins is normal.

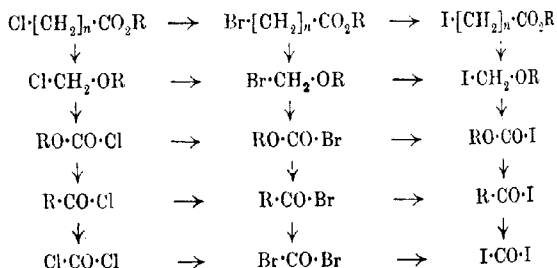
The acid bromides, like the corresponding chlorides, exhibit optical exaltation, the order being  $R \cdot COCl < R \cdot COBr < R \cdot COI$ . The atomic refraction of bromine in acid bromides is  $H_a$  9.514,  $D$  9.595,  $H_s$  9.805,  $H_v$  9.987,  $H_\beta - H_\gamma$  0.292,  $H_\gamma - H_\delta$  0.467. Among the compounds  $X \cdot CH_2(OR)$  and  $R \cdot CO \cdot X$  the optical exaltations increase in the direction of the arrows:



When substituents, such as the halogens alone or with oxygen or alkyl groups, accumulate around a carbon, nitrogen, or phosphorus atom, the optical exaltations fairly generally increase and the depression diminishes. The reverse behaviour is particularly noticeable when the atom adjacent to the central atom is attached to a number of substituents or is multiply linked. The accumulation of ethereal groups appears generally to have a depressing influence.

H. W.

**Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. II. The Spectrochemistry of Halogen and Oxygen Compounds.** A. KARVONEN (*Acad. Sci. Fennicae*, 1916, A, 10, No. 4, 1—22; from *Chem. Zentr.*, 1919, iii, 808. Compare preceding abstract).—The exaltation caused by the accumulation of chlorine and oxygen atoms has been confirmed by observations on a series of chlorinated aliphatic esters. In general, the optical exaltation diminishes when the halogen atoms in the chain are further removed from one another or from the oxygen atom. The esters of aliphatic acids containing a chlorine atom attached to the terminal carbon atom appear to exhibit a slight optical depression. In the annexed combinations, the optical exaltations increase in the direction of the arrows:



H. W.

**Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. III. Spectrochemical Behaviour of the Esters of Normal Acids of the Oxalic Series.**

A. KARVONEN (*Acad. Sci. Fennicae*, 1916, A, 10, No. 5, 1—20; from *Chem. Zentr.*, 1919, iii, 811. Compare preceding abstracts).—Optical investigation of the methyl and ethyl esters of the oxalic series shows that the exaltation diminishes uniformly as far as the succinic esters with increasing separation of the carboxyalkyl groups. The oxalic esters show slight exaltation, malonic esters behave normally, and the succeeding esters exhibit a slight depression with a tendency to increase in refraction towards the higher members. Esters of suberic and sebacic acids behave similarly to other esters of the oxalic series.

H. W.

**Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. IV. Spectrochemical Behaviour of Ether-Esters,  $\text{RO} \cdot [\text{CH}_2]_n \cdot \text{CO}_2\text{R}$ .**

A. KARVONEN (*Acad. Sci. Fennicae*, 1916, A, 10, No. 6, 1—14; from *Chem. Zentr.*, 1919, iii, 811. Compare preceding abstracts).—The following substances have been investigated: ethyl and methyl carbonates, methyl methoxyacetate, ethyl ethoxyacetate, propyl propoxyacetate, methyl  $\beta$ -methoxypropionate, ethyl  $\beta$ -ethoxypropionate, propyl  $\beta$ -propoxypropionate, methyl  $\alpha$ -methoxypropionate, and ethyl  $\alpha$ -ethoxypropionate. In the case of the lower fatty esters, the optical values diminish when a hydrogen atom of the acid radicle is replaced by an alkyloxy-group. The optical depressions diminish as the ethereal oxygen atom and the carbonyl group become more distantly separated in the alkyloxy-aliphatic esters.

H. W.

**Secondary Spectrum of Hydrogen.** T. R. MERTON (*Proc. Roy. Soc.*, 1920, [A], 96, 382—388).—The spectrum of hydrogen at 1 mm. pressure, and of hydrogen in helium at 40 mm. pressure have been photographed, using a concave grating 120 cm. radius of curvature and ruled 8000 lines per cm. It is shown that the lines of the secondary hydrogen spectrum in the red and yellow regions are greatly enhanced in the presence of helium, and that other new lines appear. In the more refrangible parts of the spectrum there is little difference in the intensity of the lines in the two cases. A second class of lines is not affected at all by the presence of helium, whilst a third class diminishes in intensity and in some cases disappears entirely. It is suggested that the change in intensity under the experimental conditions may serve as a method of investigation of the secondary hydrogen spectrum. Photographs of both spectra are given over the range  $\lambda$  4300— $\lambda$  6500. A tabulated list of the lines which are not affected and of those which are enhanced in the presence of helium together with the intensities under the two sets of conditions is appended to the paper. The lines  $\lambda\lambda$  5831.26 and 5703.86 are enhanced from intensity 2 to 7,  $\lambda$  5819.60 from 2 to 8, and  $\lambda$  5812.84 from 6 to 10.

J. F. S.

**Series of Multiple Lines in the Argon Spectrum.** KNUD AAGE NISSEN (*Physikal. Zeitsch.*, 1920, **21**, 25—28).—A theoretical paper in which the lines of the argon spectrum are arranged into series. J. F. S.

**Spectra of Isotopes.** T. R. MERTON (*Proc. Roy. Soc.*, 1920, [A], **96**, 388—395).—The spectra of ordinary lead, lead from pitchblende and lead from thorite, ordinary thallium and thallium from pitchblende have been examined. An arc was produced between a tungsten button and the metal under investigation, in a bell jar at a pressure of 1 mm. The respective interference fringes produced by means of a Fabry and Perot étalon were photographed and measured by a micrometer. It is found that the line  $\lambda 4058$  in the case of pitchblende lead has a slightly greater wave-length than in the case of ordinary lead, whilst for lead from thorite, it is somewhat shorter. The measurements in the case of thallium are not conclusive because pure thallium was not isolated from pitchblende. J. F. S.

**A Relation between the Heads of Banded Spectra belonging to Different Elements of the same Group.** TOKIHARU OKAYA (*Proc. Phys. Math. Soc. Japan*, 1919, [3], **1**, 111—121).—It is shown that for the three elements gold, copper, and silver the wave-lengths of the heads of bands emitted by their molecules satisfy fairly well the linear relation  $\lambda = \alpha + \beta n$ , where  $\alpha$  and  $\beta$  are constants and  $n$  is the series of natural numbers. From this it is concluded that between the heads of the band spectra emitted by the different molecules in similar conditions there exists a simple relation when the bands diverge toward the red side. Thus, the wave-length  $\lambda$  of the head of some band of one element with reference to the corresponding one  $\lambda'$  of another element is given by the relation  $\lambda = (\alpha + \beta n)(m/m')^{1/2}(p/q)^2$ ,  $p$  and  $q$  being certain integers,  $m$  and  $m'$  the atomic weights of the elements concerned, and  $\lambda' = (\alpha + \beta n)$ . CHEMICAL ABSTRACTS.

**Spectra of Tin, Lead, Antimony, and Bismuth in a Magnetic Field.** P. A. VAN DER HAERT (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 300—312).—Using the light from a condensed spark between poles of tin, lead, antimony, and bismuth respectively, the author has examined the effect of a magnetic field of about 30,000 gauss on a number of lines of these metals. The Zeeman effect is measured for 35 lines of tin, 23 of lead, 27 of antimony, and 16 of bismuth. The measurements show deviations from those previously published by Purvis (*A.*, 1907, ii, 919), due to uncertainty in the strength of the field used by Purvis. The resolutions of the lines are fairly regularly distributed between values which are 1—1.5 times the normal resolution. Incidentally, it is shown that the antimony lines  $\lambda\lambda 4370$ , 4295, 4287, 4091, 4078, 4038, 4024, 4006, 4004, 3979, 3721, 3467, and 3460 measured by Schippers (*A.*, 1912, ii, 877), and published in Kayser's "Handbuch der Spectroscopie," do not exist. The lines are respectively

λλ 2913, 2863, 2858, 2727, 2719, 2692, 2683, 2671, 2670, 2653, 2480, 2311, and 2306. The error has arisen by Schippers mistaking lines of the third order for lines of the second order. J. F. S.

**Colour of Metallic Salts.** YUSU SHIBATA (*J. Tokyo Chem. Soc.*, 1919, **40**, 463—482).—From the spectral analysis of compounds of cobalt, nickel, and chromium the author deduces that the region of colour formation in these salts lies between the non-metallic atomic group and the metallic group which form a nucleus for the complex ions or double salts. In no case is colour developed by metallic salts without the formation of complex ions. Colourless complex inorganic salts which show strong absorption in the ultra-violet are composed of constituents which are absolutely transparent in this region. A theory is developed which leads to the conclusion that the wave-length of the light absorbed is longer the smaller is the atomic volume of the metal forming the centre of the complex. The conclusion is supported by experimental evidence in the case of correspondingly constituted complex salts of zinc, platinum, copper, tin, silver, cadmium, and mercury.

The application of the theory to chromophores in organic compounds is discussed.

CHEMICAL ABSTRACTS.

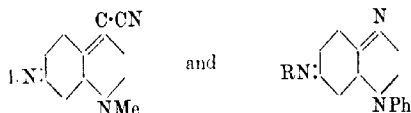
**Relation between the Visible Absorption Spectra of certain Metals in their  $M^vX_6$  and  $(M')^vX_6$  Derivatives.**

MATHEUS D'ANDRADE ALBUQUERQUE (*Revista Chim. pura applic.*, 1916, **1**, Reprint 14 pp.).—In order to verify the law of the conservation of even or odd valencies in derivatives of the same element, evidence was sought for the existence of molecules of the type  $M_2X_6$  in salts derived from sesquioxides. A number of coloured salts with colourless anions were investigated in non-dissociating solvents, or compounds containing complexes, such as  $K_2MX_6$  and  $K_3MX_6$ . Two methods were available: (1) combination of two different salts of the type  $M_2X_6$  so as to obtain a mixed salt  $MM'X_6$ ; if the properties of the latter were different from those of  $M_2X_6$  and  $(M')_2X_6$ , the difference must be attributed to linking between M and M'; (2) spectrographic evidence for some union between M and M'. The observation of the absorption spectra proved that the normal salts derived from sesquioxides always presented absorption bands, most of which were in the region where salts of the type  $MX_3$  of the same element show no absorption. When an element combines with another in different proportions, the colour of the compounds shifts towards the red end of the spectrum as the valency increases; and as the colour of sesquioxide salts is often abnormal, this must be attributed to a radicle which can only be  $M_3$ . In the iridichlorides of silver and thallium the author assumes the presence of a complex radicle containing iridium because, unlike other reddish-brown iridichlorides, the salts are blue and bluish-green respectively, that is, approximating towards the colour of  $IrCl_3$  or  $Ir_2Cl_6$ . It is observed that didymium gives a characteristic absorption spectrum differing from those of praseodymium and neodymium.

ium, which points to the existence of an atomic complex. In the majority of cases the colour of salts of the type  $M_2X_6$  is complementary to that of the salts  $MX_4$  of the same element, a property which will be discussed in a future paper. W. R. S.

**Absorption Bands in the Ultra-violet and Magnetic Birefracton.** GUSTAVE MASSOL and A. FAUCON (*Bull. Soc. chim.*, 1919, [iv], 25, 585—588).—It is shown that the substances or groups which give absorption bands in the ultra-violet also exhibit magnetic birefracton as found by Cotton and Mouton (compare A., 1910, ii, 368). W. G.

**Quinone-imide Dyes. XII. Absorption Spectra of some Cyanoacridine and Cyanopyronine Dyes.** F. KEHRMANN and M. SANDOZ (*Ber.*, 1920, 53, [B], 63—66).—In an earlier paper (A., 1918, i, 313) it was shown that the substitution of the group :C:C:N for the tervalent nitrogen atom in safranines and azoxines has practically no effect on the colour. The absorption spectra for three sets of comparable dyes have now been determined, revealing the same feature. In fact, the groups



especially may be regarded as optically equivalent. J. C. W.

**Determination of the Constitution of Coloured Substances from their Absorption Spectra. II.** F. KEHRMANN and MAURICE SANDOZ (*Helv. Chim. Acta*, 1920, 3, 104—114. Compare A., 1918, ii, 418).—The absorption spectra of the mono- and di-amino- and of the dianilino-phenazines have been examined.

Alcoholic solutions of phenazine and aminophenazine are almost colourless and orange respectively, whilst similar solutions of *s*- and 2:3-diaminophenazines are pale yellow and very light yellow; this is in accordance with the authors' theory that the introduction of an amino-group in the para-position to the nitrogen of quinone-imines or in the same position with respect to the carbon atom of triphenylmethane has a hypsochromic or bathochromic influence which depends on the basicity of the group into which it enters. The introduction of the first amino-group into phenazine considerably increases the basicity, but this is not the case with the second group. Phenylated derivatives of phenazine are slightly more red than the corresponding non-phenylated compounds, but are chiefly noticeable for the augmentation of the intensity of colour effected by introduction of the phenyl group. In general, the absorption curves of the bases do not present any striking anomalies, and the authors therefore attribute to them the orthoquinonoid structure of phenazine itself.

Mono- and di-aminophenazines have very similar absorption spectra when dissolved in fuming sulphuric acid, which closely resemble that of the di-acid salt of phenazine; they appear, therefore, to have the orthoquinonoid structure, the imino-groups having lost their auxochromic effect by conversion into amino-salts. When, however, the solutions are gradually diluted with concentrated sulphuric acid, the blood-red colour suddenly changes to green, the shade differing somewhat with the individual compound. The gradual dilution of the acid appears to cause hydrolysis of the poly-acid salts and to liberate one by one the auxochrome groups, the activity of which has been paralysed by salt-formation. Thus the green shade of the tri-acid salt of diaminophenazine gradually gives place to the violet tint of the di-acid salt and to the cherry coloration of the mono-acid salt. Since the successive transformations take place in a continuous manner without appearance of any striking anomalies, the authors ascribe the paraquinonoid constitution to the di-acid and mono-acid salts, as well as to the green tri-acid compounds.

The ultra-violet spectra of the bases and of the mono-acid salts have been examined. With the former, an absorption band is invariably observed, which becomes progressively displaced towards the visible violet as the chromogen becomes more highly substituted; it is situated at  $\lambda = 250 \mu\mu$  for phenazine, at  $\lambda = 265 \mu\mu$  for the mono- and di-aminophenazines, and at  $\lambda = 285 \mu\mu$  for dianilinophenazines. The position of the anilino-groups which has such a marked influence on the position of the bands in the visible spectrum appears to have no effect on the location of the band in the ultra-violet. The mono-acid salt of aminophenazine gives two bands in the ultra-violet, that of 1:2-diaminophenazine has one band in the visible violet ( $\lambda = 457 \mu\mu$ ), whilst the second is but slightly shifted; that of *s*-diaminophenazine shows only one band in the ultra-violet, the second having completely disappeared. The mono-acid salts of the anilinophenazines likewise only show one band in the ultra-violet ( $\lambda = 285 \mu\mu$ ). It appears, therefore, that isomeric substances with equal molecular weights give superposable spectra in the ultra-violet.

H. W.

**Photochemical Actions produced in Crystals by means of Polarised Light.** M. PADOA (*Atti R. Accad. Lincei*, 1919, [v], 28, ii, 372-377).—The author has studied the action of polarised light on crystals of cinnamic acid, *o*-nitrobenzaldehyde, and cinnamylidenemalononic acid (compare Weigert, A., 1918, ii, 344), all of which compounds undergo pronounced photochemical transformations.

After exposure to the action of light, crystals of cinnamic acid become dulled, the dimeric  $\alpha$ -truxillic acid being formed (compare Stobbe, A., 1919, i, 329). Since this action is manifest only after prolonged exposure, it may be assumed that solid solutions between the monomeric and dimeric forms are first formed; that such solutions are supersaturated is confirmed by the normal cryoscopic



behaviour of  $\alpha$ -truxillic acid in cinnamic acid solution, and melting-point measurements indicate the concentration limit of the super-saturated solutions to be 3% of the truxillic acid. No appreciably different results were obtained on exposing crystals of cinnamic acid to the action of polarised light, in the one case with the plane of polarisation parallel, and in the other normal, to one pair of parallel edges of the crystal.

When two prismatic crystals of *o*-nitrobenzaldehyde (compare Lobry de Bruyn and Jungius, A., 1903, ii, 531; Bruni and Callegari, A., 1904, ii, 545) are crossed normally and exposed in a polarising microscope to the influence of polarised light with the plane of polarisation at  $45^\circ$  to the axes of the two crystals, one of the latter undergoes change more rapidly than the other.

Results similar to, but more pronounced than, those obtained with *o*-nitrobenzaldehyde are observed in the case of cinnamylidenemalononic acid. After an exposure to the action of polarised light varying, according to the magnitude of the crystals, from one and three-quarters to three hours, part of the crystal, with its axis perpendicular to the plane of polarisation, is violently detached and often projected to a distance; in some cases, however, only transverse segmentations appear in the crystals, such occurring earlier and in greater number in the crystal mentioned. Subsequently, crystalline nodules of the dimeride make their appearance. Here too it may be assumed that solid solutions of the dimeride in the monomeride are first formed, these solutions being so unstable as to produce a condition of tension in the crystals, and consequent explosion. The partial transformation of the monomeride into the dimeride may be followed by means of the melting point, which shows marked lowering even before any change in the crystal is apparent.

Weigert's conclusions are criticised, and arguments are advanced in support of the view that phototropy is to be classed among the real photochemical phenomena. T. H. P.

**Behaviour of Fehling's Solution in Light.** IVAN BOLIN and GUNNAR LINDER (*Zeitsch. physikal. Chem.*, 1919, **93**, 721—736).—The action of light from a carbon arc on Fehling's solution in glass and quartz vessels has been studied at  $15^\circ$  and  $25^\circ$ . The amount of cuprous oxide precipitated was estimated by titration with potassium permanganate. The light reactions were compared with the reactions occurring in the dark. It is shown that in glass vessels the reaction has no temperature-coefficient, and that there is no evolution of gas. The velocity of reaction is proportional to the time during which the solution has been illuminated, and on removing the light the reaction ceases. In quartz vessels, the reaction has a temperature-coefficient 1.2, and after about three hours' illumination there is an evolution of gas. The velocity of the reaction increases with the time of illumination, and when the light is removed, the reaction continues for some time. The difference in the course of the reaction in glass and quartz vessels is explained

as follows. In quartz vessels, in addition to the photochemical reaction, an ordinary chemical reaction also takes place. This reaction is caused by substances produced in the photo-reaction. Both reactions produce cuprous oxide, the chemical reaction increasing more as reducing substances are produced photochemically. Consequently, the total amount of cuprous oxide produced increases progressively with the time. On shutting off the light, the reaction continues until all the reducing substances have been used up. The reaction is more pronounced in quartz vessels, because these allow light of smaller wave-length than  $350\text{ }\mu\mu$  to enter the liquid, and it is due to these waves that the reducing substances are produced from the tartrate in the solution.

J. F. S.

**The Recoil of  $\alpha$ -Particles from Light Atoms.** L. B. LOEB (*Phil. Mag.*, 1919, [vi], **38**, 533–541).—An account is given of an attempt to verify the conclusion of Rutherford, namely, that in collisions between  $\alpha$ -particles and light atoms, the number of atoms projected straight forward within an angle of  $10^\circ$  from that of the  $\alpha$ -particle is ten to thirty times that calculated from Darwin's theory of point charges, by examining the number of  $\alpha$ -particles recoiling after collision with light atoms. The conditions necessary to ensure success and overcome the numerous difficulties are worked out, but the results are provisional and indecisive for lack of sufficient time. They indicate that for aluminium the abnormalities found by Rutherford for nitrogen and hydrogen begin to show themselves, but the experimental difficulties were not overcome for lighter elements, such as carbon. The range of the  $\alpha$ -particle deflected at  $105^\circ$  from aluminium was found to be below  $3.6\text{ cm.}$ , as is to be expected if the laws of energy and momentum apply to these close encounters.

F. S.

**Passage of Corpuscular Rays through Material and the Constitution of the Atom.** I. R. SEELIGER (*Jahrb. Radioaktiv. Elektronik*, 1919, **16**, 19–65).

—A theoretical paper in which the author discusses the work of many investigators on the passage of  $\alpha$ - and  $\beta$ -rays through material. The consideration is concerned with the individual processes and changes brought about by the passage of a corpuscular ray through an atom or a molecule. These changes are subdivided into changes in the moving particle: (i) direct conveyance of kinetic energy to the atom, and (ii) emission of electromagnetic radiation; and into changes in the atom: (i) direct gain in kinetic energy, (ii) emission of electromagnetic radiation, (iii) emission of secondary corpuscular radiation, and (iv) chemical changes.

J. F. S.

**Connexion between Collision Ionisation and the Energy of Ionisation of Neutral Molecules.** J. FRANCK, P. KNIPPING, and THEA KRÜGER (*Ber. Deut. physikal. Ges.*, 1919, **21**, 728–732).

—The ionisation steps of hydrogen have been investigated. It is shown that definite ionisation occurs at  $11.5 \pm 0.7$  volts,  $17.1 \pm 0.25$

5\*.

volts, and  $30.4 \pm 0.5$  volts. The first step corresponds with the formation of  $H_2^+$ , and the measurements show that an ion with considerably larger diameter is formed at 11.5 volts than at 17 or 30 volts. At  $13.6 \pm 0.7$  volts there is an emission of ultra-violet light, the potential  $17.1 \pm 0.25$  volts corresponds with the ionisation of the atom into a normal, and a positive ion and an electron, and the potential  $30.4 \pm 0.5$  volts corresponds with ionisation of the atom into two positive ions and two electrons. These results go to show that the Bohr atom model of hydrogen is not strictly in keeping with the facts.

J. F. S.

**Apparatus for the Separation of Radium Emanation and its Estimation Electroscopically.** J. E. UNDERWOOD and HERMAN SCHLUNDT (*Trans. Amer. Electrochem. Soc.*, 1918, **34**, 203—209).—An apparatus is described by means of which radium in various ores and concentrates may be estimated. The material is either boiled with concentrated sulphuric acid or fused with a mixture of alkali carbonates or with sodium hydrogen sulphate in one part of the apparatus, and the emanation stored in a mercury burette in another part of the apparatus. The emanation is kept for ten minutes in the burette to allow the thorium emanation to decay, and is then passed into the electroscope, where it is measured in the usual way. Using this method, Brazilian monazite is shown to contain  $0.794 - 0.812 \times 10^{-7}$  gram radium per gram; Indian monazite,  $0.1017 - 0.1025 \times 10^{-7}$  gram radium per gram. J. F. S.

**Comparison of the Ionisation Currents due to Equal Quantities of Radium Emanation in Different Types of Electroscopes.** T. H. LEANING, HERMAN SCHLUNDT, and JULIUS E. UNDERWOOD (*Trans. Amer. Electrochem. Soc.*, 1916, **30**, 365—378).—The authors have compared the ionisation currents obtained with several types of electroscopes (Lind, Wulf quartz fibre, Fontactometer, Duane and Laborde, and Randall), and find that, with the exception of the Randall rectangular electroscope, the measured currents have lower values than the values calculated by the formula of Duane and Laborde,  $I = K(I - C.S/V)$ . In some cases, the values were 18—22% too low. The experiments show that the reduction factor,  $C$ , of Duane and Laborde's formula has specific values for ionisation chambers of definite dimensions. J. F. S.

**Absorption of Radium Gamma Rays.** K. W. F. KOHLBRAUSCH (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, **126**, IIa, 683—704).—The results of the investigation are given in the following table, where  $K_1$ ,  $K_2$ , and  $K_3$  are the three components of the complex  $\gamma$ -rays from radium:

*Absorption Coefficients  $\mu_1$ ,  $\mu_2$ , and  $\mu_3$ .*

Absorber.	$K_1$	$K_2$	$K_3$
Lead .....	0.545	1.4	4.6
Zinc .....	0.327	0.57	1.44
Iron .....	0.356	0.63	3.00
Aluminium .....	0.127	0.23	0.57

The ratio of the energies measured by ionisation currents is, for these three components,  $K_3:K_2:K_1=1:6:8$ . The absorption measurements show that the influence of secondary radiation is extremely important.

CHEMICAL ABSTRACTS.

**The Hard Secondary Gamma Rays from Radium.** K. W. F. KOHLRAUSCH (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, **126**, IIa, 705—720).—In a previous paper (compare preceding abstract) the author made a careful series of measurements of the absorption of the  $\gamma$ -rays of radium in various substances. In these experiments, the importance of secondary radiation was indicated. The present paper deals with this secondary radiation, which is shown to have a high penetrating power. When the  $\gamma$ -rays pass through matter, a very hard type of secondary radiation ( $\mu_{\text{Fe}}=0.545 \text{ cm.}^{-1}$ ) is produced. The author compares the observed total energy of the secondary radiation with the calculated values for varying thickness of screen. The observations are in good agreement with theory.

CHEMICAL ABSTRACTS.

**Absorption of Gamma Rays from Radium.** K. W. F. KOHLRAUSCH (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, **126**, IIa, 887—913).—The results are given of an extensive series of measurements of the absorption coefficients of radium  $\gamma$ -rays in different substances.

CHEMICAL ABSTRACTS.

**The Chemical Character of Protoactinium [Ekatan-talum]. I. Separation of Protoactinium from Pitchblende.**

OTTO HAHN and LISE MEITNER (*Ber.*, 1919, [B], **52**, 1812—1828).

—The raw material for the preparation of protoactinium is the insoluble residue, consisting principally of silica, from pitchblende after treatment of the mineral with nitric acid. By repeated extraction with nitric acid, all the radioactive substances, including radium, can be dissolved, and the residue left with a very feeble  $\alpha$ -activity, due chiefly to protoactinium. It is recommended to add from  $\frac{1}{2}\%$  to 1% of tantalum oxide to the pitchblende residue and to heat it with a little concentrated sulphuric acid and excess of 40% hydrofluoric acid in a platinum capsule covered with a platinum dish containing cold water to serve as a condenser, then to dilute and filter through a paraffined funnel, evaporate the filtrate, and ignite the residue gently, which renders the tantalum oxide containing the protoactinium insoluble in acids. An addition of a few milligrams of thorium and of lead nitrates to the hydrofluoric acid serves to keep traces of ionium, uranium-X, and radiolead from passing through the filter with the tantalum. The ignited tantalum oxide is boiled with aqua regia to remove iron, arsenium, etc., leaving the tantalum undissolved.

The Rutherford-Boltwood ratio of 8% for the actinium branch series would, neglecting correction for difference of range, lead to an  $\alpha$ -activity of proto-actinium 4% of that of the uranium in the mineral from which it is extracted. This is found to be much too high. The protoactinium was separated from known amounts of

pitchblende by three different methods, detailed below, and the  $\alpha$ -activity of the preparation extracted per gram of mineral was found to be the same, within 10%, in six experiments, from which, after applying a correction for the range, it is calculated that only 3% of the atoms of uranium disintegrating pass through the protoactinium, actinium series. The three methods consist of: (1) fusion of the pitchblende with sodium hydrogen sulphate, followed by treatment of the insoluble residue with hydrofluoric acid, as already detailed; (2) treatment of the very finely divided mineral with hydrofluoric acid and sulphuric acid, in which the main part of the protoactinium passes into solution directly; (3) treatment of the mineral very similarly to that described already for the residue. Full details of the chemical operations and charts are given showing, in each case, the distribution of the radio-elements in the successive stages of treatment. Tantalum oxide was always added to the mineral, and elaborate care taken, more of this material being added and separated from each of the separate parts to remove protoactinium, to ensure that all was separated. Finally, as a test, a known amount of previously prepared protoactinium preparation was added to pitchblende, and the result showed that no loss, exceeding 5%, occurred in the course of the chemical treatment.

The low percentage of the actinium series operates against sufficient protoactinium being present in uranium minerals for isolation like radium. Its period of average life can only be fixed within the limits of 1200 and 180,000 years at present, which correspond with weights in the mineral of 1.5% and 22.5% of the weight of contained radium. So far, efforts to concentrate it from tantalum have failed. It is suggested that an examination of the amount of protoactinium in old uranium preparations might throw further light on the period, and uranium preparations of known age of uranium, not less than 100 to 200 grams, are appealed for. The 3% ratio agrees with the ratio found for the relative activities of uranium- $X_1$  and uranium- $F$ . It is pointed out that protoactinium with atomic weight about 230 and place in the periodic table beyond thorium, of atomic weight 232, furnishes probably another example similar to that of tellurium and iodine. F. S.

**The Origin of Actinium.** OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1919, 20, 529–533. Compare preceding abstract).—The paper contains some further details of the methods employed for determining the relative  $\alpha$ -activity of the preparations measured. F. S.

**Determination of the Half-life Periods of Thorium and Actinium Emanations.** R. SCHMID (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, 126, IIa, 1065–1079).—The author describes a method which is the same in principle as that used by Leslie and Perkins. Measurements were also made by Rutherford's method, in which the ionisation current is measured at different points along a tube

through which the emanation is flowing at a known rate. A third method employed is due to Mache. The mean results of the investigation are as follows: half-life period for thorium emanation  $54.6 \pm 0.03$  secs.; for actinium emanation  $3.92 \pm 0.015$  secs.

CHEMICAL ABSTRACTS.

**The Age of Thorium Minerals.** R. W. LAWSON (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, 126, IIa, 721-739).—The paper deals with the end-product of the thorium series in the light of the atomic weight results of Hönigschmid and others. It is shown that the age, determined from the Th/U and Pb/U ratios, may be between 8 and 300 million years. The minerals employed came from Devon, Brevig, and Norway. The possible origin of the large discrepancy in age is discussed. Thorium minerals from Ceylon give a range from 138 to 506 million years.

CHEMICAL ABSTRACTS.

**Electrolytic Dissociation Theory.** GEORGE SENTER (*Trans. Faraday Soc.*, 1919, 15, 3-9).—An introductory paper to a discussion of *The Present Position of the Theory of Ionisation* (see following abstracts), in which the author summarises certain investigations on electrolytes in solution, namely, hydration, deviation of strong electrolytes from the law of mass action, and the chemical activity of ions and non-ionised molecules. It may be regarded as established that ions and undissociated molecules may simultaneously undergo chemical change, and that in the catalytic activity of strong acids the non-ionised molecule plays a part as well as the hydrogen ion.

J. R. P.

**Electrolytic Dissociation.** SVANTE ARRHENIUS (*Trans. Faraday Soc.*, 1919, 15, 10-17).—The author summarises the present evidence in favour of the dissociation theory of solution under eleven headings: (1) Evidence from analytical chemistry. (2) Additive properties. (3) The diffusion of electrolytes. (4) The electric conductivity of solutions. (5) Colours of solutions. (6) Ostwald's law. (7) Non-aqueous solutions. (8) Ostwald's law for salt solutions in water. (9) The freezing point of aqueous solutions. (10) Deviations in concentrated solutions. (11) Velocity of reaction.

J. R. P.

**Present Position of the Ionisation Theory: Reactions of both the Ions and Molecules of Acids, Salts, and Bases.** S. F. ACREE (*Trans. Faraday Soc.*, 1919, 15, 18-26).—Mainly an historical account of attempts to elucidate the so-called "abnormal salt effect" of dissolved electrolytes. Results on the inversion of sucrose and other reaction velocities are explained by assuming that molecules, as well as ions, are active. The acid molecules are found to be two or three times more active than the hydron in the case of hydrochloric, hydrobromic, and nitric acids, as measured by the hydrolysis of sucrose. A similar conclusion was reached for the hydrolytic activity of alkalis. The activity of molecules is also deduced from a study of the action of alkyl haloids in alcoholic

solution on phenoxides. Another cause of abnormal salt effect is solvation, studied by Lapworth. Several tables of values of the velocity constants of ions and molecules, deduced from the author's results and from re-interpretation of those of other workers, are given.

J. R. P.

**The Bearing of Migration Data on Conduction in Solutions. The Electrochemistry of Sodium Iodide in Acetone.**

JAMES W. MCBAIN and F. C. COLEMAN (*Trans. Faraday Soc.*, 1919, 15, 27—46).—When the sum of the movements of both ions is equal to the total current, the solvent cannot be appreciably dissociated. This is the case in aqueous solutions. Hypotheses to the contrary are therefore invalidated. The migration data for solutions of sodium iodide in acetone, and of silver bromate in diethylamine, show that, even in highly concentrated solutions, the solvent does not conduct appreciably. The evidence of the migration data shows that conductivity is only an approximate measure of the degree of dissociation, since the migration ratio almost invariably increases with the concentration, a change ascribed to solvation. The calculation of conductivities at infinite dilution from extrapolation of dilution formulae to infinite dilution, or from the assumption of the law of mass action at infinite dilution, are regarded with disfavour. The molecular weight of sodium iodide in acetone, determined by the boiling-point method, is normal.

J. R. P.

**The Determination of the Ionisation of an Aqueous Solution.**

W. R. BOUSFIELD (*Trans. Faraday Soc.*, 1919, 15, 47—73).—A summary of the methods used by the author in calculating the ionisation of an electrolyte in aqueous solutions. Ionisation is assumed to be the result of the interaction of associated water molecules with the molecules of the salt, whereby  $(\text{H}_2\text{O})_3$  and  $\text{H}_2\text{O}$  molecules react with the salt to produce  $(\text{H}_2\text{O})_2$  molecules and hydrated ions. The application of the law of mass action then gives equations which give good results for a large class of strong electrolytes at high dilutions, and in the case of the alkali chlorides give good results in concentrated solutions. On account of varying hydration, it is assumed that the transport numbers require correction. This, however, cannot at present be carried out except by the method of trial and error. Stress is laid on the part played by the solvent, which is assumed to exist in associated forms, the proportions of which vary with the concentration of the solution.

J. R. P.

**Correction of the Transference Numbers of the Ions of an Electrolyte.**

W. R. BOUSFIELD (*Trans. Faraday Soc.*, 1919, 15, 74—80).—On the assumption that the volumes of the ions in solution are unequal, the correction necessary in the ordinary method of calculating the relative ionic mobilities from the transport numbers is found. The corrections are inappreciable at concentrations less than normal.

J. R. P.

**Some Aspects of the Electrolytic Dissociation Theory.**

NILRATAN DHAR (*Trans. Faraday Soc.*, 1919, 15, 81—93).—By a discussion of recent work on electrolytes, including molecular-weight determinations, Kohlrausch's rule, freezing points, osmotic pressures, heats of neutralisation of acids and bases, and absorption spectra, the conclusion is drawn that the theory of non-ionisation proposed by Snethlage (*A.*, 1915, ii, 615, 825) is not tenable.

J. R. P.

**The Hydration of Ions.**

HENRY J. S. SAND (*Trans. Faraday Soc.*, 1919, 15, 94—97).—In his calculations of the radii of ions, Bousfield adopts a radius for the water molecule which leads to a value for Avogadro's constant over twenty times that adopted in the same calculations. The values for the ionic radii deduced from Stokes's law do not agree with those derived from other calculations. It is believed that it is incorrect to apply the law of Stokes to molecular magnitudes.

J. R. P.

**Some Recent Investigations on the Dilution Law.**

J. R. PARTINGTON (*Trans. Faraday Soc.*, 1919, 15, 98—121).—In the case of weak electrolytes the law of mass action applies with greater accuracy than to any other case yet investigated. The viscosity correction has been applied in a very arbitrary manner by many investigators, and the author believes that in dilute solutions it is unnecessary. The equation deduced by Szyskowski (*A.*, 1915, ii, 616) gives very accurate results for strong electrolytes, and renders unnecessary the arbitrary alterations made by Kraus and Bray (*A.*, 1913, ii, 914) in the accurate experimental values of Kohlrausch and Maltby (*A.*, 1900, ii, 61). It is shown that the theory proposed by Ghosh (*A.*, 1918, ii, 348, 392, 423) is not in accordance with the experimental results of the latter observers, since it requires equal ionisations at equal dilutions for all electrolytes of the same type, whereas differences are found. It is concluded that the law of mass action applies to strong electrolytes at great dilution.

J. R. P.

**Variation of Electrical Conductivity of Electrolytes with Increase of Concentration.**

ALFRED W. PORTER (*Trans. Faraday Soc.*, 1919, 15, 122—125).—The empirical equation of Kohlrausch,  $1 - \alpha = \text{const.} \times c^{\frac{1}{2}}$ , is shown by a graphical method to hold over a large range. The index  $n$  of Storch's equation,  $\alpha/(1 - \alpha)^n = K V^{1-n}$ , is practically the same for potassium chloride as for sodium sulphate, in spite of the difference in valency. This equation has the form required by the law of mass action for a possible reaction, although the particular reaction which makes  $n = \frac{2}{3}$  (van't Hoff) has not yet been identified. The assumption of electrical action between the ions would lead to diminution of the ionisation  $\alpha$  with concentration at a greater rate than required by the law of mass action, whereas the opposite effect is actually found. If the law of mass action holds good at great dilution, it is necessary to explain the transition from this to the other laws which hold



at increased concentrations. A possible equation is  $a^2(1+ba/V)/(1-a)[1+c(1-a)/V]=\text{const.}$ , where  $b$  and  $c$  are additional constants.

J. R. P.

**The Resistance of an Electrolytic Cell.** EDGAR NEWBERRY (*Trans. Faraday Soc.*, 1919, **15**, 126—136).—That part of the irreversible resistance of an electrolytic cell which is concerned in the transfer of the current from electrode to electrolyte has been studied in a number of cells. Transfer resistance is greatest when gases are liberated at the electrodes, considerable when gaseous ions are utilised in carrying the current, although not liberated at the electrodes, and negligibly small when the current is carried by metallic cations and by anions which readily dissolve the anode. Conditions favourable for high transfer resistance are low current density, low temperature, polished surfaces, and high over-voltages. Those conditions which affect the nature of the surfaces affect also the transfer resistance. Transfer resistance is due to the mechanical resistance (pressure and frictional) which opposes the penetration of gaseous ions into the surface of the electrodes. Measurements of electrical conductivity are liable to serious error if transfer resistance is not perfectly eliminated, and there is reason to fear that this has not been done in determining some of the conductivity data at present available.

J. R. P.

**Effect of Interionic Forces in Electrolytes.** S. R. MILNER (*Trans. Faraday Soc.*, 1919, **15**, 148—151).—Chemical forces, which cause the association of two ions into a molecule, diminish extremely rapidly with the distance, and become negligible at very small separations of the ions, whereas electrical forces between the ions fall off comparatively slowly. The ordinary derivation of the law of mass action for electrolytes assumes that interionic forces become negligible for finite separations of the ions. These forces, however, would cause a reduction of osmotic pressure and of molecular lowering of freezing point. The application of the inverse square law leads to general agreement with the observed freezing-point curves. The conductivity should be proportional to the osmotic pressure of the free ions, that is, those possessing sufficient kinetic energy to escape from their attracting neighbours.

J. R. P.

**Ionisation and the Mass Law.** H. M. DAWSON (*Trans. Faraday Soc.*, 1919, **15**, 152—153).—The deviations from the law of mass action in the case of strong electrolytes are ascribed mainly to changes in the ionising power of the solvent by the highly polar solutes.

J. R. P.

**The Abnormality of Strong Electrolytes.** JNANENDRA CHANDRA GHOSH (*Trans. Faraday Soc.*, 1919, **15**, 154—163).—The author does not agree with the criticisms of Partington (see above). The deviation from his theory shown by some electrolytes is ascribed to hydration of the ions.

J. R. P.

### Equilibrium between Bromine and Potassium Bromide Solutions at 0°.

GRINNELL JONES and MINER LOUIS HARTMANN (*Trans. Amer. Electrochem. Soc.*, 1916, **30**, 295—326).—Measurements of the equilibrium between bromine and water and between bromine and potassium bromide solutions at 0°, and of the specific conductivity of the solutions have been made. Calculations by the method of successive approximations based on the results show that the following reactions occur: (i) bromine dissolves as  $\text{Br}_2$ ; (ii)  $\text{Br}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}' + \text{Br}' + \text{HBrO}$ ; (iii)  $\text{KBr} + \text{Br}_2 \rightleftharpoons \text{KBr}_3$ ; (iv)  $\text{KBr} + 2\text{Br}_2 \rightleftharpoons \text{KBr}_5$ . A saturated solution of bromine in water at 0° has the composition  $\text{Br}_2 = 0.2539$  mol. per litre;  $\text{H}'$ , 0.001085;  $\text{Br}'$ , 0.000126;  $\text{Br}_3'$ , 0.000628; and  $\text{Br}_5'$ ,  $0.000331$ . The hydrolysis constant,  $K_h = (\text{H}')(\text{Br}')(\text{HBrO})/\text{Br}_2 = 5.7 \times 10^{-10}$ , the equilibrium constant,  $K_3 = \text{Br}' \times \text{Br}_3'/\text{Br}_2' = 0.051$ ; and the equilibrium constant,  $K_5 = \text{Br}' \times \text{Br}_5'^2/\text{Br}_2' = 0.0246$ . The partition-coefficient of  $\text{Br}_2$  between water and carbon tetrachloride after correcting for hydrolysis is  $D = 21.018 + 2.831C$ , where  $C$  is the concentration of  $\text{Br}_2$  in the carbon tetrachloride. By means of these constants the concentration of each ion may be calculated in any solution containing known amounts of potassium bromide up to 0.1N and bromine up to saturation. The conductivity of a series of solutions of potassium bromide from 0.001N to 0.1N has been determined at 0°. When extrapolated to infinity by Noyes' method, these results give 83.8 for  $\Delta_\infty$ , and if the ionic conductivity of  $\text{K}'$  is 40.1,  $\text{Br}'$  has the value 43.7. From the data for the specific conductivity of solutions of potassium bromide containing bromine it follows that the ionic conductivity of  $\text{Br}_3'$  is 23.5 and of  $\text{Br}_5'$ , 16.3. J. F. S.

**Corrosion of Metals by Acids.** OLIVER P. WATTS and NEWTON D. WHIPPLE (*Trans. Amer. Electrochem. Soc.*, 1917, **32**, 257—284).—The rate of corrosion and solution of iron, zinc, zinc amalgam, mercury, cadmium, tin, lead, copper, gold, silver, tin amalgam, and lead amalgam by means of hydrochloric acid, sulphuric acid, perchloric acid, phosphoric acid, and acetic acid, and also by solution of sodium hydroxide and a series of salts, has been determined. The effect of a number of oxidising agents on the rate of solution has also been investigated. The following oxidising agents were used: hydrogen peroxide, sodium arsenate, ferric sulphate, ferric chloride, potassium dichromate, potassium chlorate, mercuric chloride, potassium permanganate, potassium nitrate, chromic anhydride, nitric acid, potassium bromide, sodium nitrite, and potassium iodide. The authors confirm the view previously put forward (*ibid.*, 1912, **21**, 340) that the protective effect of arsenic on the corrosion of iron by sulphuric acid is due to polarisation by hydrogen. This view is confirmed by the facts that the corrosion of iron by acids when the metal was protected by arsenic was greatly accelerated by oxidising agents and arsenic does not protect iron from attack by corrosive agents which do not evolve hydrogen by their action. Amalgamation protects zinc from corrosion by acids because the discharge potential of hydrogen on mercury exceeds the potential on zinc. Protection by arsenic and mercury are alike in their

nature. Tin and lead are very slowly dissolved by non-oxidising acids, although their potentials are such as would cause their ready solution in acids, if it were not for the unusually high discharge potential of hydrogen on them. Removal of hydrogen by an oxidising agent causes these metals to dissolve readily in acids that otherwise corrode them very slightly. Corrosion by acids, of metals below hydrogen in the electrochemical series, namely, copper and silver, has been brought about by the presence of oxidising agents. The statement that the corrosion of amalgamated zinc in dilute sulphuric acid is accelerated in a vacuum is shown to be incorrect. By removing the depolarising oxygen of the air, reduction of pressure retards corrosion, not only of amalgamated zinc, but of other metals the solution of which is hindered by a polarising film of hydrogen. With respect to their corrosion the metals examined may be classified as follows: (a) Metals the potentials of which exceed the discharge potential of hydrogen on them; these dissolve readily in acids except such as form insoluble salts. (b) Metals the potentials of which are less than the discharge potential of hydrogen on them; these dissolve readily in acids only in the presence of oxidising agents. Gold and platinum are not readily attacked by acids in general, even when these contain oxidising agents. The superiority of nitric acid over other acids as a solvent for metals is due to its being at the same time an acid and an oxidising agent, which enables it to dissolve metals of the second class, which non-oxidising acids are unable to do. Oxygen is necessary for success in cyaniding gold ores because in dilute cyanide solutions gold is a metal of the second class. Measurements of the discharge potential of hydrogen in solutions of potassium cyanide and sodium hydroxide, and experiments on the corrosion of metals in the latter, lead to the conclusion that the above classification, the action of oxidising agents, and protection by other metals will apply to the dissolving of any metal in any electrolyte from which it displaces hydrogen when passing into solution. The above classification of metals according to the relative magnitude of their potentials in comparison with the discharge potential of hydrogen on them applies not only to the solution of metals, but also to their electrolytic deposition. Plating baths for depositing metals of the first class cannot be strongly acidified without causing the deposition of much hydrogen in place of an equivalent amount of metal; but a large proportion of acid may be added to solutions for the deposition of metals of the second class without greatly lowering the current efficiency through the deposition of hydrogen.

J. F. S.

**Heat of Hydration of Gaseous Atomic Ions.** K. FAJANS (*Ber. Deut. physikal. Ges.*, 1919, **21**, 709—713. Compare this vol., ii, 12, 21).—A theoretical paper in which a correction of the heat of hydration of the hydrogen ion is made; in place of the previously published figure  $H^+ = 362$  Cal. per gram ion, the more correct, but still approximate, value 260 Cal. per gram ion is substituted. The term "hydration of ions" is more fully defined.

The term is not intended to indicate the formation of hydrates of the ions of definite stoichiometric composition, but rather that, due to the electrostatic charge of the ions, the oppositely charged part of the polar water molecule is turned toward the ion, and this in its turn exerts an attractive force on the next molecule. This type of dielectric polarisation proceeds continuously in the water surrounding the ion. The heat of hydration increases with decreasing volume of the gaseous ion, and reaches an exceedingly large value with the hydrogen ion.

J. F. S.

**Affinity of Halogen Atoms for Electrons and the Energy of Ionisation of the Hydrogen Haloids.** K. FAJANS (*Ber. Deut. physikal. Ges.*, 1919, **21**, 714—722. Compare preceding abstract).

—A theoretical paper in which, making use of the principles previously published, the author calculates the energy change, in the form of a development of heat, which results from the combination of the halogen atoms with an electron. It is shown that the combination occurs with considerable loss of energy, but that the amount decreases with increasing atomic weight; the values found are in Cals.: chlorine 116, bromine 87, and iodine 81. The wave-length of the spectrum line brought about by this combination is calculated by means of the formula  $\epsilon = h\nu = h \times 3 \times 10^{10} / \lambda$ , in which  $\epsilon$  is the energy change and  $\lambda$  the wave-length in Ångström units. The following values are obtained: chlorine 2440, bromine 3350, and iodine 3490. By the same method of calculation, the work of ionisation of the hydrogen haloids has been obtained. The heat of combination of a gaseous hydrogen ion with a gaseous halogen ion is found to be: chlorine 322, bromine 310, and iodine 300 Cal. Using the formula  $I' = 1000U / 96,500 \times 0.2388$ , in which  $I'$  is the ionisation potential and  $U$  the energy change, the ionisation potential has been calculated, and the following values obtained: hydrogen chloride 14.0 volts, hydrogen bromide 13.4 volts, and hydrogen iodide 13.0 volts.

J. F. S.

**Electron Affinity of Gases.** K. FAJANS (*Ber. Deut. physikal. Ges.*, 1919, **21**, 723—727. Compare preceding abstracts).—In an earlier publication, Franck (*A.*, 1910, ii, 817) attributes the loss

of mobility of negative ions in the presence of oxygen and other gases to the combination of the gas atoms with electrons, and he formulates a potential series of the various gases. This question is discussed in the present paper. It is shown that the collision of an electron with a gas molecule effects the change represented by one of the equations: (1)  $X_2 + \ominus = X + X^-$ ; (2)  $X_2 + 2\ominus = 2X^-$ . For the halogens, the potential of the change is calculated, and the following values obtained: equation (1), chlorine -0.44 volt, bromine -1.78 volts, and iodine -1.96 volts; equation (2), chlorine -5.47 volts, bromine -5.55 volts, and iodine -5.47 volts. In the case of the hydrogen haloids, particularly hydrogen chloride, the change  $HX + \ominus = H + X^-$  is supposed to occur, and this, on calculation, yields the potentials: hydrogen chloride +0.39 volt, hydrogen bromide -0.09 volt, and hydrogen iodide -0.53 volt.

Both considerations explain the formation of gas ions from electrons and atoms without the necessity of assuming a specific electron affinity.  
J. F. S.

**Theory of Heat Change.** F. HABER (*Ber. Deut. physikal. Ges.*, 1919, **21**, 750—768).—A theoretical paper in which the author discusses the theory of heat change in connexion with (i) hydration energy of gaseous ions, (ii) energy of dissociation of salt vapours and ionisation potential of metal cations, and (iii) lattice energy and ultra-violet characteristic frequencies.  
J. F. S.

**Affinity of the Halogen Atoms towards Electrons.** M. BORN (*Ber. Deut. physikal. Ges.*, 1919, **21**, 679—685. Compare Born, A., 1919, ii, 214; Fajans, this vol., ii, 12).—A theoretical paper in which, based on the theory put forward previously by the author and Fajans (*loc. cit.*), the affinity of the halogen atoms for electrons is calculated. The values  $E$ , the energy of combination of an atom with an electron,  $Z$ , the energy of dissociation of an atom into ion and electron, and  $D$ , the heat of dissociation of a diatomic gas, are calculated, and the following numerical values in Cals. obtained: fluorine,  $Z = -26$  (mean); chlorine,  $Z = -62$  (mean),  $D = 57$ ,  $E = 119$  Cals., or 5.16 volts; bromine,  $Z = -61$ ,  $D = 23$ ,  $E = 84$  Cals., or 3.64 volts; iodine,  $Z = -59$ ,  $D = 18$ ,  $E = 77$  Cals., or 3.33 volts. It is shown, also, that the wave-length corresponding with the energy can be calculated on the basis of the quantum theory. The following wave-lengths in Ångström units are obtained: chlorine,  $\lambda = 2380$ ; bromine,  $\lambda = 3360$ ; iodine,  $\lambda = 3680$ .  
J. F. S.

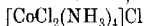
**Cuprous Oxide Photo-chemical Cell.** THEODORE W. CASE (*Trans. Amer. Electrochem. Soc.*, 1917, **31**, 351—364).—The action of light on one electrode of the cell  $\text{Cu}|\text{Cu}_2\text{O}|\text{aqueous copper formate} + \text{formic acid}|\text{Cu}_2\text{O}|\text{Cu}$  has been investigated. It is found that an *E.M.F.* up to 0.085 volt can be obtained and a current of 0.003 ampere if the metal plates are  $20 \times 3.2$  cm. in size. By arranging the cell on a rotating disk, so that the copper plates are alternately illuminated, an alternating current of various amplitudes and frequencies may be obtained. The action of the cell indicates that, under proper conditions, its life may be continuous, and that its elements will not disintegrate. The action of the cell is compared to the resistance change of the mineral cuprite when exposed to ultra-violet light. The contrast between the *E.M.F.* effect of cuprous oxide and cupric oxide is discussed. The action of the cuprous oxide photochemical cell is explained on the basis of the oxidation of cuprous oxide to cupric oxide in light. It is shown that there is no relation between the sign of the light action and the colour of heated copper plates.  
J. F. S.

**Determination of Hydrogen-ion Concentration.** JOHN W. M. BUNKER (*J. Biol. Chem.*, 1920, **41**, 11—14).—A modification of a bubbling electrode used in a closed vessel is fully described.

The apparatus is designed to meet the requirements of quick, accurate determinations in large numbers, and has given satisfactory results.  
J. C. D.

**Phenomenon after Anodic Polarisation. II.** A. SMITS, G. L. C. LA BASTIDE, and TH. DE CRAUW (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 296—299. Compare this vol., ii, 8).—It was previously shown that, on interrupting the current by which iron is polarised anodically, the potential of the iron falls, passes through a minimum, and then reaches the original value. This is due to diffusion changes, which affect the ratio  $Fe''/Fe'''$ . A similar phenomenon is now observed for nickel which has been anodically polarised. In solutions of nickel chloride, the minimum is reached in less than three seconds, whilst in the case of nickel sulphate, the change is much more prolonged. On cathodic polarisation of iron, the reverse phenomenon is observed, namely, the potential of the iron passes through a maximum and then falls to the normal value. This is to be expected if the explanation offered in the case of anodically polarised iron is correct.  
J. F. S.

**Polarisation Tension and Constitution of Complex Cobalt Compounds.** NILRATAN DHAR and G. URBAIN (*Compt. rend.*, 1920, **170**, 106—108).—The polarisation tension of a complex salt depends, not only on the constitution of the complex ion, but also on the nature of the ion which accompanies it. Thus, in the series starting with  $[Co(NH_3)_6]Cl_3$ , the replacement of ammonia by water causes a diminution in the tension, whereas in the series



the contrary holds good. The replacement of a molecule of water by a halogen in such a compound as  $[Co(NH_3)_5H_2O]Cl_3$  causes a rise in the polarisation tension. Further, in the purpureo-salts, the tension is higher when the purpureo-complex contains a more negative radicle. The replacement of a chlorine atom by a nitro-group or of two chlorine atoms by a carbonato-group causes a lowering of the polarisation tension. The marked rise in the tension following on the substitution of an hydroxy-group for a chlorine atom is in agreement with the fact that these complex compounds are only stable in alkaline media.  
W. G.

**The Polarisation in Solutions of Iron.** W. ALBERT NOYES, jun. (*Compt. rend.*, 1920, **170**, 177—180. Compare this vol., ii, 9).—Nernst's formula,  $A = 0.0002T/m_1n_1$ , for calculating the value of  $A$  in the equation  $Ep = A \log_{10} I + B$ , giving the potential of an electrode traversed by a current, does not apply to the polarisation of solutions of ferrous salts, but none the less gives values proportional to the experimental values.  
W. G.

**Electrolytic Behaviour of Tungsten.** WALTER E. KOERNER (*Trans. Amer. Electrochem. Soc.*, 1917, **31**, 221—255).—The potential of tungsten in  $N$ -solutions of potassium cyanide, sodium hydroxide, potassium hydroxide, ammonium hydroxide, sulphuric

acid, hydrochloric acid, potassium nitrate, nitric acid, potassium fluoride, potassium chloride, potassium bromide, potassium sulphate, and potassium iodide has been measured against certain standard electrodes at 25°. The results show that tungsten does not behave as an insoluble electrode, but sends ions into the solutions with velocities which vary with the different solvents. Tungsten has a lower potential in *N*-alkalis than in *N*-acids, and a lower potential in *N*-acids than in *N*-salts. The following *E.P.* values (*H*=0) are calculated from the experimental results; alk solutions were normal: potassium cyanide, -0.647 volt; sodium hydroxide, -0.316 volt; potassium hydroxide, -0.315 volt; ammonium hydroxide, -0.238 volt; sulphuric acid, 0.193 volt; hydrochloric acid, 0.256 volt; potassium nitrate, 0.300 volt; nitric acid, 0.311 volt; potassium fluoride, 0.522 volt; potassium chloride, 0.563 volt; potassium bromide, 0.589 volt; potassium sulphate, 0.719 volt; and potassium iodide, 0.733 volt. A further series of *E.M.F.* measurements were made for tungsten in saturated solutions of tungstic acid in *N*-solutions of hydrochloric, sulphuric, and nitric acid respectively. The following values are obtained: hydrochloric acid, 0.317 volt; sulphuric acid, 0.313 volt; and nitric acid, 0.317 volt. The following combinations were also measured:

$W | W(OH)_6, N-H_2SO_4 || N-H_2SO_4 | W$ ,  
0.117 volt;  $W | W(OH)_6, N-HCl || N-HCl | W$ , 0.057 volt; and  
 $W | W(OH)_6, N-HNO_3 || N-HNO_3 | W$ , 0.009 volt. The *E.M.F.* values obtained give the relative solubilities of tungstic acid in *N*-acid solutions. Analytically, the values were found to be: sulphuric acid, 0.02281 gram  $WO_3$  per litre; hydrochloric acid, 0.01067 gram  $WO_3$  per litre; and nitric acid, 0.00025 gram  $WO_3$  per litre. The anodic behaviour of tungsten has been investigated, and it is shown that in solutions of tungsten in acids it behaves as a cation, whilst in solutions of tungsten in alkalis it behaves as an anion. Tungstic acid goes into solution in acids and alkalis as an electrolyte, and not as a colloid. Tungsten dissolves anodically in aqueous and non-aqueous solutions of alkalis, acids, and salts. Under specified conditions, tungsten becomes passive when used as anode in aqueous and non-aqueous solutions of acids, bases, and salts. In aqueous solutions of alkalis and non-aqueous solutions of acids, bases, and salts, tungsten only becomes passive at high current densities (2 amperes per sq. dcm.). In aqueous solutions of acids and salts, the passive condition is assumed by tungsten at low current densities, and only at extremely low current densities will it remain active in these solutions. The passivity of tungsten is due to adherent films of hydrated oxides of tungsten. The films may be readily dissolved and the passivity destroyed. The hydrated oxide films appearing on the anode vary in colour from brown through blue to yellow. The degree of passivity varies with the colour of the films. The electrochemical equivalent of tungsten was found to be 0.3173 mg. per coulomb, a value very closely in agreement with the theoretical value. A number of experiments on the use of tungsten in storage cells are recorded. It is found

that the potential difference between the brown oxide (+) and the blue oxide (-) is 0.75 volt.

J. F. S.

**Electrical Endosmose and Adsorption.** T. R. BRIGGS, H. L. PIERSON, and H. S. BEYNETT (*Trans. Amer. Electrochem. Soc.*, 1917, **31**, 257—270).—Using a modified form of Perrin endosmometer, which obviates the error produced by the evolution of gas at the electrodes and permits the use of diaphragms composed of powdered solids, the authors have determined the effect of the applied *E.M.F.* on the rate of flow of the liquid for the case of water with a glass diaphragm. In this case, the liquid flowed to the cathode, and the rate was found to be in keeping with Perrin's law for *E.M.F.* values lying between 530 and 100 volts. The effect of temperature on the rate of flow, using water and asbestos diaphragms and cellulose in boiled water, was determined at temperatures from 18° to 67°. It is shown that the product, rate  $\times$  viscosity<sup>-4</sup>, is practically constant. The flow of liquid in acid and alkaline solutions was investigated with alundum diaphragms, when sharp reversals were obtained, which are in keeping with Perrin's results. With glass diaphragms, no such reversal of direction was observed. The effect of barium ions on the rate of flow to the cathode in alkaline solutions is to reduce it much more than would an equivalent quantity of univalent ions. In acid solutions, barium ions have little effect, but sulphate ions reduce the rate much more than chloride, nitrate, or acetate ions. This with alundum and carborundum diaphragms. A number of experiments with dyes in *N*/500-solutions of hydrochloric acid and sodium hydroxide are described. It is shown that acid dyes (eosin, crystal ponceau) in alkali travel to the cathode, whilst basic dyes (safranin and methylene-blue) in acids travel to the cathode; acid dyes in acids and basic dyes in alkalis give indefinite results; alundum diaphragms were used in these experiments. The relationship between dyeing and electrical endosmosis tends to confirm the adsorption theory.

J. F. S.

### Chemistry of the Flaming Arc, in Relation to Luminescence.

WILLIAM ROY MOTT (*Trans. Amer. Electrochem. Soc.*, 1917, **31**, 365—390).—The light produced by flaming arcs containing various substances, and the relative volatility of refractory substances have been investigated. It is shown that there is no case of a blue arc shell. In every case except barium and vanadium, the arc core is blue or violet and the shell green, yellow, or red. Hence the light from the shell in every case but barium and vanadium is of longer wave-length than that of the arc core. The non-metallic elements, fluorine, chlorine, bromine, iodine, oxygen, sulphur, and nitrogen do not give elemental spectra, but fluorine, chlorine, oxygen, and nitrogen give the spectra of compounds in a carbon arc. The elements phosphorus, arsenic, and boron give only a few ultra-violet lines in the carbon arc. The easily reduced metals except those of the iron group yield no arc shell. The low energy of reac-



tion at high temperatures explains this lack of light. The most electropositive elements give the most markedly coloured luminous shells, especially where more than one valency stage is characteristic of the element at high temperatures. With yttrium oxide, the crater on the bead alone gives a green shell, which replaces the usual red shell obtained with the crater partly on the bead and partly on the carbon. Zirconium oxide gives a yellowish-white shell. The colour is probably due to hot solids, as zirconium carbide is less volatile than platinum, and its oxidation would give an extremely non-volatile oxide. Metallic zirconium is fairly volatile. In nearly every case with a carbon arc the flow of material is from positive to negative. With mixtures of salts of potassium, rubidium, and cesium fluoride respectively with calcium fluoride a strong blast also comes from the negative crater which causes a unique dimness near the negative part of the arc. A dim, large positive crater can often be produced by nearly all salts of potassium, rubidium, and cesium and by oxy-salts of sodium. This, with the effect on cyanogen bands and arc length may be explained by the reaction  $\text{KF} + \text{C}_2\text{N}_2 = \text{KCN} + \text{CNF}$ , and others necessary to return by oxidation to potassium fluoride, carbon dioxide, and nitrogen. A dim negative crater is most easily produced by barium salts volatilised from the positive crater. Glucinum oxide is the least volatile of the oxides which are so insulating as to prevent cratering, such as oxides of the alkaline earths, aluminium oxide and silica. The oxides of yttrium, zirconium, thorium, and the other rare earths show cratering. Tungsten is by far the least volatile of the known elements, and this is followed by tantalum. The light of a yellow flame arc is due to reactions involving calcium fluoride, calcium oxide, calcium carbide, and metallic calcium.

J. F. S.

#### Magnetism of the Metalammine Compounds. ERNST

ROSENBOHM (*Zeits. f. physikal. Chem.*, 1919, **93**, 693—720).

—The magnetic susceptibility of a very large number of metallic ammine derivatives has been determined at 16—20° by means of a Curie torsion balance. The metals investigated were cobalt, platinum, rhodium, iridium, ruthenium, zinc, nickel, copper, and chromium. The ammine derivatives of cobalt, platinum, iridium, rhodium, zinc, and ruthenium are, except in the case of some of the cobalttriammines, diamagnetic. The diamagnetism is greatest in hexammine salts of cobalt, somewhat less in the pentammine derivatives, very much less in the tetra-ammine derivatives, and least in the triammine derivatives of cobalt. In the last class of compounds it is found occasionally that paramagnetism is exhibited. The same regularity is observed when the whole or a portion of the ammonia group is replaced by ethylenediamine or propylenediamine. The entrance of one or more ionogen residues into the sphere of the metallic atom is shown to be followed by a decrease in the diamagnetism in the case of all the diamagnetic metallic amines investigated. In the case of platinum it is shown that the susceptibility and molecular magnetism of

bivalent platinum is less diamagnetic than is the case with quadrivalent platinum. Further, as in the case of the electro-conductivity, in passing from hexammino- to hexacido-derivatives, the magnetism passes through its extreme value with those compounds which have no ionogen acid residue. The ammine derivatives of nickel, copper, and chromium are paramagnetic. In the case of the chromium derivatives it is shown that the magnetic susceptibility and the molecular magnetism are least in the hexammine derivatives and increase steadily to the triammine derivatives. As in the case of the cobalt derivatives the extreme value occurs with those derivatives which contain no ionogen acid group. The examination of the geometrical isomerides of the derivatives of cobalt, platinum, and chromium indicates that magnetically the *cis*- and *trans*-forms of a given compound cannot be differentiated. At the same time it is shown that the measurement of the magnetic susceptibility is a very sensitive method of testing the purity of these isomerides. In the case of the optical isomerides of cobalt and chromium, it is shown that the *d*- and *l*-forms have the same susceptibility, whilst the racemate has a different value. In most cases the susceptibility of the racemate is smaller than that of the active isomerides, but this is not always so. In the case of the co-ordination isomerides of cobalt and chromium, it is found that the susceptibility is not alike, but in most cases the two values are not very different. The greatest difference is found in the case

$$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{C}_2\text{O}_4)_3] \chi \cdot 10^6 = 18.80;$$

$[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{C}_2\text{O}_4)_3] \chi \cdot 10^6 = 13.75$ . The difference observed between the co-ordination isomerides and the other types of isomerides is probably due to the fact that the two nucleus atoms are magnetically opposed to one another, the one acting diamagnetically and the other paramagnetically. An examination of the magnetic influence of the nucleus atom shows that metalamines, with a metal valency which is stable in the normal salts, possess a susceptibility of the same order as the normal salts, whilst metalamines, with a metal valency which is unstable in the normal salts, may have a susceptibility very different from that of the normal salts, and it may even be of the opposite sign. Measurements of the polynuclear cobalt and chromium amines show that these compounds are quite normal in their magnetic relationships. The molecular magnetism is calculated from Pascal's formula,  $M = \Sigma A + 1$  (A., 1911, ii, 91), and the values compared with the present measurements. It is found that both sets of values are remarkably close. The magnetic properties are considered in connexion with the magnetone, and it is shown that in accordance with Weiss's theory the magnetone number is always a whole number. J. F. S.

**A Thermoregulator with the Characteristics of the Beckmann Thermometer.** R. B. HARVEY (*J. Biol. Chem.*, 1920, 41, 9-10).—The instrument can be set easily at any temperature desired between  $-20^\circ$  and  $+250^\circ$ . The electrical contacts are placed so that small temperature changes will make or break the circuit. When run on test in an air-bath with a standard Beckmann

thermometer and vigorous stirring, the air temperature was regulated to within  $\pm 0.004^\circ$ .  
J. C. D.

**Specific Heat of Sulphuric Acids, Nitric Acids, and their Mixtures.** PAUL PASCAL and M. GARNIER (*Bull. Soc. chim.*, 1920, [iv], 27, 8—18).—Using an electrical method of heating, the authors have determined the specific heats of binary mixtures of sulphuric acid and water containing from 10 to 100% of sulphuric acid, of binary mixtures of nitric acid containing from 10 to 98% of nitric acid, of binary mixtures of nitric and sulphuric acids, and of ternary mixtures of nitric and sulphuric acids and water. The results are set out in detail, and a graph with trilinear co-ordinates combines the data.  
W. G.

**Latent Heat and Surface Energy.** G. RUDORF (*Phil. Mag.*, 1920, [vi], 39, 238—239).—A criticism of Hammick's paper under the above title (A., 1919, ii, 389), in which it is shown that using more accurate values for  $\gamma$  (surface tension),  $\sigma$  (molecular diameter), and  $L_i$  (internal latent heat), the values of  $\gamma V/J\sigma$  and  $L_i/6$  give results which are widely divergent in the case of argon. The values calculated by the author are 302 and 240 respectively, instead of 226 and 214 calculated by Hammick.  
J. F. S.

**Critical Constants. Critical Temperature of Hydrogen Bromide.** E. MOLES (*J. Chim. Phys.*, 1919, 17, 415—424).—A criticism of Fielding's work (compare A., 1919, ii, 45) in which the author supports the law of Guldberg and Guye as to the relationship between the absolute critical temperature and the absolute boiling point/760 mm.

For hydrogen bromide the author finds experimentally the value  $89.80^\circ$  for the critical temperature, and the value as calculated by Guldberg and Guye's rule is in reasonably close agreement with this.

He further indicates that Fielding's formula (*loc. cit.*) for calculating the critical pressure gives results considerably higher than those found by experiment in the cases of hydrogen chloride and hydrogen sulphide.  
W. G.

**Form and Regularities of the Vapour Pressure Curve.** E. WERTHEIMER (*Ber. Deut. physikal. Ges.*, 1919, 21, 692—708).—A theoretical paper in which it is shown that the previously published vapour-pressure formula,  $p + Ap^2 = CT^n$  (*ibid.*, 1919, 21, 435), contains in itself five approximation laws dealing with the saturation state, namely, Dühring's rule of constant boiling-point difference, the law of analogous state, Trouton's rule of normal heat of vaporisation, the constancy of the van der Waals' number ( $f$ ) at the critical point, and the Nernst equation for calculating chemical constants. These expressions are all developed from the above formula, and examined by means of a large number of previously published examples.  
J. F. S.

**Vapour Pressure Regularities.** W. HERZ (*Zeitsch. Elektrochem.*, 1919, **25**, 408—409. Compare A., 1919, ii, 218).—According to the theory of corresponding states, the proportionality factor  $a$  in van der Waals's equation,  $\log \pi_0/p = a(\delta_0/T - 1)$ , where  $\pi_0$  is the critical pressure,  $\delta_0$  the critical temperature (in absolute units), and  $p$  and  $T$  corresponding values of pressure and temperature, should for all normal substances have the constant value 3. The value of  $a$  has been calculated for the elements hydrogen, nitrogen, oxygen, mercury, argon, krypton, xenon, chlorine, and bromine, and in most cases it is nearer 2 than 3, and is always less than 3. In vertical series the value increases with the atomic weight of the element. The value of the constant has also been calculated for the hydrocarbons pentane to decane, acetic and propionic acids, a number of alkyl esters of fatty acids, and some alkyl chlorides, in some cases for a number of different temperatures. In all these cases its value is close to 3. It may rise or fall with increasing temperature, and in most cases shows a distinct rise as a homologous series is ascended. Associated liquids show a greater value for  $a$  than similarly constituted non-associated liquids. Thus the value for water is greater than that for hydrogen sulphide, and that for ammonia greater than that for phosphine. E. H. R.

**Relative Volatilities of Refractory Materials.** WM. ROY MOTT (*Trans. Amer. Electrochem. Soc.*, 1918, **34**, 255—295).—Ten arc methods of ascertaining the relative volatilities of metals, carbides, oxides, nitrides, fluorides, chlorides, and sulphides are suggested and to some extent developed. The most rigid method depends on the least volatile material remaining as the residue when distilling mixtures. For materials boiling above the boiling point of iron saturated with carbon (3500°) a series of boiling points has been estimated on a triple basis of reference, namely, reference to the curves for iron for equal atomic amounts of material, fractional distillation series, and position of deposition at the negative arc crater. The boiling points in the series are: iron saturated with carbon, 3500°; silica, 3500°; palladium, 3600°; carbon, 3700°; alumina, 3700°; chromium carbide, 3800°; vanadium carbide, 3900°; rhodium, 4000°; platinum, 4050°; uranium carbide, 4100°; ruthenium, 4150°; lanthanum oxide, 4200°; titanium carbide, 4300°; yttrium oxide, 4300°; columbium carbide, 4300°; zirconium oxide, 4300°; thorium oxide, 4400°; iridium, 4400°; osmium, 4450°; molybdenum carbide, 4500°; yttrium carbide, 4600°; thorium carbide, 5000°; zirconium carbide, 5100°; tantalum carbide, 5500°; tungsten carbide, 6000°. Tungsten allows carbon to distil rapidly through its molten carbide, which probably surrenders carbon vapour exactly as copper oxides surrender oxygen. The boiling point of tungsten is estimated at 6000° and that of tantalum at 5500°. Zirconium carbide is the least volatile carbide, and is followed by thorium carbide. Thorium oxide is the least volatile oxide, whilst the white and yellow oxides of zirconium are nearly as non-volatile. The least volatile non-cratering oxide is glucinum oxide (b. p. 3900°), which is left as a final residue in fractional

distillation of its mixtures with barium oxide, strontium oxide, calcium oxide, magnesium oxide, silica, and alumina. From the crater distances at positive and negative, the boiling points of the more common refractory oxides are estimated as follows: barium oxide, 2000°; titanium oxide, below 3000°; chromium sesquioxide, 3000°; calcium oxide, 3400°; silica, 3500°; magnesia, 3600°; alumina, 3800°; and glucinum oxide, 3900°. "Smoke time" estimates of boiling points are given for several oxides, sulphides and halogen salts. The figures are only roughly approximate. The volatility of oxides follows the increasing order: potassium, sodium, lithium, vanadium, boron, barium, strontium, manganese, iron, cobalt, nickel, chromium, titanium, silicon, calcium, magnesium, aluminium, erbium, cerium, neodymium, lanthanum, zirconium, and thorium. The characteristic oxide is intended in every case. Boron nitride sublimes at about 3000°. As an addendum to the paper is added a bibliography of work on the volatilisation of refractory materials, and where in these papers figures are given for boiling points and melting points these are recorded. A further addendum deals with the ratio of the melting point to the boiling point. These values are given for practically the whole of the elements, and it is shown that with the exception of the metals of the first group of the periodic system the ratio abs. b. p./abs. m. p. = ca. 1.8. J. F. S.

**Glass Rectifying Column especially suitable for the Rectification of Liquid Mixtures and the Recovery of Volatile Solvents.** W. ELSNER (*Chem. Zeit.*, 1920, **44**, 11-12).—

The apparatus consists of a glass column 50 mm. in diameter and filled with glass balls, the surfaces of which are ground or etched. A perforated plate at the bottom of the column serves as a support for the balls, and the latter are of three sizes, the lower part of the column containing the largest balls, whilst the smallest balls form the uppermost layers. The top of the column is connected with a small glass dephlegmator provided with a water jacket, which is supplied from a constant-level reservoir, and above the dephlegmator is a still-head carrying a thermometer and a side-tube, which is connected with a condenser. All parts of the apparatus are connected together by means of ground-in joints.

W. P. S.

**Saturation Pressure, calculated from the Temperature, Latent Heat of Vaporisation, and the Molecular Volume of the Liquid by means of Maxwell's Distribution of Velocities Law.** K. K. JÄRVINEN (*Zeitsch. physikal. Chem.*, 1919, **93**, 743-753).—

A theoretical paper wherein equations are deduced by means of which the saturation pressure may be calculated. These equations have the form

$$c_z = c_3/c = \sqrt{(2W_i + 3RT)/M} : \sqrt{3RT/M} = \sqrt{(2W_i/3RT) + 1},$$

and  $z = p/p_a$ , in which  $z$  is the number of molecules which have a velocity  $c$ ,  $c_z$  is the mean velocity of the molecules,  $p$  is the

saturation pressure,  $p_a$  the internal pressure, and  $W_i$  the internal latent heat of vaporisation. The remaining symbols have their usual significance. The expression has been tested on the substances oxygen, nitrogen, benzene, ether, *n*-pentane, toluene, and methyl butyrate, and a fair agreement with fact obtained.

J. F. S.

**Molecular Attraction. IV.** K. K. JÄRVINEN (*Zeitsch. physikal. Chem.*, 1919, **93**, 737—742. Compare preceding abstract, and A., 1913, ii, 293; 1915, ii, 251; this vol., ii, 90).—A theoretical paper in which the author recalculates the constants used in the formulae previously published (*loc. cit.*). It is found for monatomic molecules that  $n=5$  and  $\alpha=55.06$ .  $W_i.v^{\frac{1}{3}}=41.30.C_a.v^{\frac{1}{3}}/\alpha$ . In the case of polyatomic molecules, the molecular attraction is represented by the expressions  $F=m^2k/(r-\beta r_0)^n=m^2k/(v^{\frac{1}{3}}-\beta v_0^{\frac{1}{3}})^n$ . From this equation, the following expressions are deduced:

$$a=(n-1)/3.W_i(v^{\frac{1}{3}}-\beta v_0^{\frac{1}{3}})^{n-1}=Ca(v^{\frac{1}{3}}-\beta v_0^{\frac{1}{3}})^n/v^{\frac{1}{3}}.$$
 and  $C_a/\alpha.W_i=(n-1)/3.v^{\frac{1}{3}}/(v^{\frac{1}{3}}-\beta v_0^{\frac{1}{3}})$ . In these expressions, the symbols have the meaning previously applied to them,  $r_0$  is the smallest distance between the molecules, and  $v_0$  the smallest volume;  $n=5$  and  $\beta=0.242$ , whence  $C_a/\alpha.W_i=4/3 \times 1.27=1.69$ . A number of substances on which the formulae have been tested give the constant 1.69, and agree most nearly with the value  $n=5$ . J. F. S.

**Method of Calculating the Limits in Physico-chemical Phenomena.** MAURICE FRUÐHOMME (*J. Chim. phys.*, 1919, **17**, 377—382).—The method previously employed for calculating the critical temperature in terms of the surface tension (compare A., 1919, ii, 183) is shown to be applicable for calculating the density at absolute zero as a function of the temperature in the case of gases, and it is shown that, as in the case of liquids, the density at absolute zero is four times the critical density. The critical pressure may also be calculated as a function of the temperature, subject to a correction of  $8^\circ$ , the calculated value being too high. W. G.

**Molecular Condition of Liquids and Solutions.** ERNST KRÖBER (*Zeitsch. physikal. Chem.*, 1919, **93**, 641—692).—Density determinations have been made at  $25^\circ$  of a large number of solutions of liquids in organic solvents, and of a number of solid substances in solid solvents. The number of molecules of solvent replaced by one molecule of the dissolved substance in unit volume is calculated in each case. It is shown that the number of replaced molecules is approximately equal only when the dissolved substance belongs to a closely related group, for example, the mono-substitution derivatives of benzene. In all other cases, different numbers of molecules of the solvent are replaced; the respective figures are approximately in the same proportion as the molecular volumes, and the relationship is only slightly dependent on the nature of the solvent and the concentration of the dissolved substance. The behaviour of solutions of solids at various temperatures has been

investigated. The volume changes accompanying the solution of liquids is small, and is not specific either in the case of solvent or dissolved substance. In the case of solids dissolved in liquids, the positive volume changes are larger, and in general appear to be due to a change in the state of aggregation. In most cases, a characteristic behaviour is observed, both with the solvent and the dissolved substance. The coefficient of compressibility and the coefficient of expansion run parallel with the mean atomic concentration and the reciprocal of the mean atomic volume. In homologous series, the atomic concentration, corresponding with constant atomic volume, is nearly constant at the boiling point, and for all substances which contain only carbon, hydrogen, and oxygen the value fluctuates only between very narrow limits. It appears possible, from the properties of a mixture, particularly from the coefficient of expansion, to decide whether a contraction or an expansion will take place. In the very large number of cases examined, only three cases were exceptional to the rules formulated, and in all probability these cases were abnormal, because of a chemical reaction between the components.

J. F. S.

**Viscosity Measurements.** O. FAUST (*Zeitsch. physikal. Chem.*, 1919, **93**, 758—761).—The influence of the diameter of the tube on the viscosity of liquids has been investigated in connexion with the method of viscosity measurements made by determining the time required for a bubble of air to rise through a measured length of the liquid. It is shown that  $Q = \pi(r^2 - r_1^2)$ , in which  $r$  is the radius of the tube,  $r_1$  the radius of the air bubble, and  $Q$  the cross-section of the liquid between the bubble and the tube. Since  $(r - r_1)$  is constant and  $r + r_1 \approx 2r$ ,  $Q = 2\pi r \times C$ , where  $C$  is a constant. The formula is tested with a viscid oil with tubes of various diameters, and the measured time compared with the calculated time. It is shown that with wider tubes (18—24 mm.) the calculated and observed results agree, but with narrower tubes (16—12 mm.) there is an increasing divergence with decreasing diameter. This is due to the fact that the error introduced by placing  $r + r_1 \approx 2r$  is greater in the case of narrow tubes than in the case of wider tubes. It is also shown that in the case of wider tubes, the time required for the ascent of the bubble is independent of the size of the bubble, whilst the same is almost true with narrower tubes.

J. F. S.

**The Welding of Solid Powders under Pressure.** TONI VON HAGEN (*Zeitsch. Elektrochem.*, 1919, **25**, 375—386).—An extensive series of experiments is described on the cohesive properties of pure powdered inorganic substances under pressure. The substances examined include the oxides, sulphides, sulphates, halogenides, nitrates, and carbonates of many metals, including both anhydrous and hydrated forms of the salts. Fine-grained particles were found to cohere better than coarser, and for most experiments the substance was ground to pass a sieve of 25 meshes per sq. mm. The

powder was subjected, for most experiments, to a pressure of 560 kilos. per sq. cm. in a screw press, and the tablets formed were examined by inspection, and, where possible, by determining their hardness or crushing strength. The substances showing the best cohesion gave tablets which appeared homogeneous. Among these were the halogenides of the alkali metals and silver and hydrated calcium chloride. The next class gave tablets with smooth surfaces and pulverulent bodies, this class including the hydrated sulphates of aluminium, zinc, cobalt, and sodium, many nitrates and sulphides, and the oxides of lead. Most of the oxides gave powdery bodies of low crushing strength, whilst the anhydrous sulphates of potassium, calcium, strontium, barium, and lead, and the carbonates of cadmium, barium, and lead showed no cohesion at all. Generally, substances of very high melting point and very hard substances show little cohesion. A cohesive substance mixed with a non-cohesive substance improves the binding properties of the latter, but quantitative experiments on the hardness of mixed tablets showed that this was not proportional to the composition. In the case of cohesive substances, increasing pressure increases the density of the tablet, rapidly at first, then slowly as the maximum is approached. The maximum may rise to the true density of the crystalline substance, as in the case of gypsum, or it may approach very nearly to this value, as with sodium and potassium chlorides.

The experiments show that there is a close relation between the crystalline form of a substance and its behaviour under pressure. Those substances which give the most homogeneous bodies under pressure are those which have plastic crystals, that is, the crystals of which contain glide-planes and are deformable without losing their structure. The above substances, which give, under high pressure, tablets having almost the maximum possible density, have been shown to have plastic crystals. On the other hand, the crystals of such substances as quartz and barium sulphate show no trace of plasticity, and their powders show no cohesive properties. [See also *J. Soc. Chem. Ind.*, 1920, 189A.] E. H. R.

**Absorption of Gases by Charcoal. I. Variations due to Heat Treatment, Pre-equilibrium Effects.** HARVEY B. LEMON (*Physical Rev.*, 1919, **14**, 281—292).—The rate at which coconut-shell charcoal absorbs air, and the total amount it can absorb, may be widely varied by varying the heat treatment. This paper considers the case in which the mass of air used is less than that required for saturation. Increase in activation is produced by repeated exhaustions at 650°, each exhaustion being followed by an absorption of air at the temperature of liquid air. Decrease in activation results if a temperature of 800—900° is used. Two hypotheses to account for this, (1) the clogging of the pores by heavy hydrocarbons, removed by flushing out with gas, and (2) the alteration in the fineness of the carbon from the point of view of a saturated solution of carbon in liquid gas, are discussed, but found inconclusive, particularly inasmuch as removal of the heavy hydro-



carbons by light petroleum, alcohol, and acetone causes loss in efficiency.

CHEMICAL ABSTRACTS.

**Absorption of the so-called Surface Active Substances by Various Absorbents.** LEONOR MICHAELIS and PETER RONA (*Kolloid Zeitsch.*, 1919, **25**, 225—229).—Comparative absorption experiments have been carried out with charcoal, kaolin, cosmosil (a commercial silicic acid preparation), talc, amorphous silicon, ferric hydroxide, freshly precipitated manganese dioxide, calomel, barium sulphate, and calcium carbonate as absorbents for acetone, tributyrin, heptyl alcohol, and octyl alcohol. It is shown that no carbon-free absorbent has a power of absorption that even approaches the absorptive power of charcoal for surface active non-electrolyte substances. In most cases there is no absorption, in others only the merest trace of absorption takes place. Talc comes next to charcoal in its absorption of these substances. J. F. S.

**Osmosis and Diffusion of Ions through a Polarised Septum. Physical Methods for the Study of Cellular Nutrition.** PIERRE GIRARD (*J. Chim. Phys.*, 1919, **17**, 383—408).—A résumé of work already published (compare A., 1908, ii, 456; 1909, ii, 463, 537; 1911, ii, 860; 1914, ii, 718; 1919, i, 419, 461) and a reply to Hamburger (compare A., 1917, ii, 562). W. G.

**Theory of Solution and Suspension.** RICHARD ZSIGMONDY (*Kolloid Zeitsch.*, 1920, **26**, 1—10).—A theoretical paper in which the significance of the terms "solution" and "suspension" is discussed at length. J. F. S.

**Physical Chemical Analysis of Metallic Oxide Sols.** WOLFGANG PAULI (*Kolloid Zeitsch.*, 1920, **26**, 20—23).—Polemical. An answer to Zsigmondy's theory of solutions and suspensions (preceding abstract), which is based on the work of Pauli and Matula (A., 1917, ii, 563). J. F. S.

**Nomenclature of Colloids.** G. WEISSENBARGER (*Kolloid Zeitsch.*, 1919, **25**, 230).—The author points out that the term "gel" is applied both to jellies and to the products of coagulation. He suggests that the term gel should be retained and used only in connexion with jellies, and that the products of coagulation should be termed *coagels*, thereby implying that they belong to the group of coarse, disperse colloids. J. F. S.

**Rôle of Valency in Coagulation by Electrolytes, particularly in the Case of the Suspensoids.** WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1920, **26**, 28—39).—A theoretical paper in which the various views put forward in connexion with the part played by the valency of the electrolyte ions in the coagulation of colloids is critically discussed. J. F. S.

**Coagulation of Clay and the Protective Effect of Humic Acid.** SVEN ODÉN (*J. Landw.*, 1919, 67, 177—208).—An extensive review is given of previous work on clay suspensions as regards their aggregation, sedimentation, disintegration, swelling value, and nature of individual particles. Experiments were made by the author with suspensions of two clays of different character, purified by dialysis, and diluted with conductivity water to about 1% strength. Varying amounts of colloidal humic acid were added to 10 c.c. of each suspension, and the effect on coagulation noted. It was found that the minimum amount required to produce a protective effect on the addition of ammonium nitrate solution as coagulant was 0.065 mg. in one case and 0.14 mg. in the other. On varying the coagulant, it was found that much larger amounts of humic acid were required to prevent coagulation with barium nitrate and cesium chloride than with ammonium nitrate and lithium chloride. The author concludes that the protective effect of humic acid is of the same order as that of other colloids, but that it is greatly affected by the electrolyte concentration, owing to the extreme sensitiveness of colloidal humic acid to electrolytes. The effect appears to be specific for different clays and electrolytes, so that a proper explanation of the effect is still uncertain. It is clear, however, that it depends on an absorption of the protective substance by the particles to be protected.

J. H. J.

**Non-, Uni-, and Bi-variant Equilibria. XIX.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 22, 318—322. Compare A., 1917, ii, 454).—A further theoretical paper dealing with the conditions of equilibrium in non-variant, uni-variant, and bi-variant systems. The present paper deals with the equilibria of  $n$  components in  $n+1$  phases.

J. F. S.

**Characteristic Case of Rhythmic Crystal Arrangement.** M. HORSÄSS (*Zeitsch. physikal. Chem.*, 1919, 93, 754—757).—A few drops of the  $N/10$ -sodium hydroxide which had been used to absorb the carbon dioxide produced in the combustion of artificial graphite was allowed to evaporate on a microscope slide. The crystals formed, when magnified 500 times, showed a striking rhythmic, concentric arrangement. Each series of rings commences from a crystal nucleus, around which circles of crystals 0.002 mm. apart are formed. In all other cases of combustion of coal, lignite, and wood, the crystals produced from the sodium hydroxide wash-bottle exhibited the usual dendritic forms.

J. F. S.

**The Rate of Decomposition of Malonic Acid.** CYRIL NORMAN HINSHELWOOD (*T.*, 1920, 117, 156—165).

**Mechanism of the Addition of Hydrogen to Unsaturated Glycerides in the Presence of Finely Divided Nickel.** R. THOMAS (*J. Soc. Chem. Ind.*, 1920, 39, 10—18T).—The rate of hydrogenation of olive oil (iodine value, 86) by means of hydrogen

in the presence of finely divided nickel has been determined at 120°, 150°, and 180°. As the olive oil contained 7% of linolin, equations are deduced for the rate of addition of hydrogen by mixtures of unsaturated glycerides. The reaction between pure hydrogen at constant pressure and a single unsaturated glyceride takes place according to the equation for reactions of the first order. The more highly unsaturated glyceride linolin absorbs hydrogen very much faster than olein. The rôle played by the catalyst is discussed from the results of experiments on the influence of pressure of hydrogen and of temperature on the velocity of reaction. It is found that the rate of saturation of olein (with three double bonds) is proportional to  $p^2$ , where  $p$  is the pressure of hydrogen. This is in keeping with the view that hydrogen becomes active through its absorption by the catalyst, with a dissociation of the hydrogen molecules into atoms. The temperature-coefficient of the velocity constant is small; an increase of 10° in temperature over the range 120–180° increases the velocity 1.13 times. This suggests a photochemical reaction, the molecules of olein being brought into an active condition by absorption of infra-red radiation emitted by the catalyst. The mode of action of gaseous catalyst poisons is illustrated and discussed. Such action may be a purely physical one, or it may be chemical in the sense that the poison is capable of reacting either with or in the presence of the catalyst.

J. F. S.

**Hydrolysis of Esters of Polyhydric Alcohols.** ЕИЧИ YAMAZAKI (*J. Tokyo Chem. Soc.*, 1919, **40**, 498–514).—Denoting the five mono-, di-, and tri-acetins by

- (A)  $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\cdot\text{OAc}$ ,  
 (B)  $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OAc}$ , (C)  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\cdot\text{OAc}$ ,  
 (D)  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OAc}$ , and  
 (E)  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\cdot\text{OH}$ ,

glycerol (G) is obtained from triacetin by hydrolysis along the following routes (annexed formula).



This apparently complicated system of hydrolysis of triacetin can be studied in a simple manner, since all esters containing  $\text{R}\cdot\text{CO}\cdot\text{O}\cdot$  have approximately the same constant of velocity of hydrolysis, which is independent of the position of the acid group in the polyhydric alcohol. The constants of velocity of hydrolysis of tri- to di-acetin ( $K_1=0.00638$ ) and of di- to mono-acetin ( $K_2=0.00423$ ) by hydrochloric acid, calculated from Geitel's data (A., 1897, ii, 547; 1898, ii, 330), are compared with the velocity constant ( $K_3=0.002213$ ) for monoacetin  $\rightarrow$  glycerol. Assuming that each acetoxyl-group is hydrolysed at the same rate,  $K_1/3=K_2/2=K_3(=K)$ . The following equations are thus derived:  $c_{A_1}=c_0e^{-3Kt}$ ;  $c_{A_2}=3c_0(1-e^{-Kt})e^{-2Kt}$ ;  $c_{A_3}=3c_0(1-e^{-Kt})^2e^{-Kt}$ ; and  $c_{A_4}=c_0(1-e^{-Kt})^3$ , where the concentrations of the three acetins and of

glycerol are denoted by  $c$  with suffixes  $M_1$ ,  $M_2$ ,  $M_3$  and  $M_4$  respectively. If free acetic acid is denoted by  $c_a$ , then

$$c_a = c_{M_1} + 2c_{M_2} + 3c_{M_3} = 3c_0(1 - e^{-Kt})^3.$$

A satisfactory agreement is recorded between the calculated and the observed values of  $c_a$  at any instant. CHEMICAL ABSTRACTS.

**The Factors of Diazotisation.** E. TASSILLY (*Bull. Soc. chim.*, 1920, [iv], 27, 19—33).—Using the method previously described (compare A., 1914, ii, 256), the author has studied the rate of diazotisation of a number of amines. The reaction has been previously shown to be bimolecular. Doubling the acidity of the solution does not modify the process of diazotisation in the case of aniline. The diazotisation of sulphanilic acid is much more rapid when the concentration of the reacting solutions is increased, and it is favoured by an excess of sodium nitrite. The stability of a diazo-compound with respect to time and temperature may be studied by this method.

W. G.

**Colour Change of Congo-rubin under the Influence of Reactions and Neutral Salt Action.** HEINRICH LÜERS (*Kolloid Zeitsch.*, 1920, 26, 15—20).—The time required by solutions of congo-rubin (0.01%) to change from red to the intermediate colour between red and blue in the presence of hydrogen ions of various concentrations and in the presence of neutral salts has been determined. It is shown that with  $H' = 5.5 \times 10^{-5}$  the change is instantaneous, but with decreasing hydrogen-ion concentration the time increases rapidly until, with the value  $H' = 6.8 \times 10^{-6}$ , it is practically infinite. In the presence of a neutral salt (KCl) very small hydrogen-ion concentrations cause the change to take place very rapidly. The presence of large quantities of neutral salts increases the activity of the indicator toward hydrogen ions about seventy times. In the presence of hydroxyl ions, neutral salts decrease the activity of the indicator until, with  $OH' = 10^{-2}$ , it no longer undergoes the colour change. These changes are explained by a change in the condition of solvation of the indicator brought about by the electrolyte.

J. F. S.

**Catalysis.** MATHEUS D'ANDRADE ALBUQUERQUE (*Revista chim. pura applic.*, 1918, 3, reprint 22 pp.).—After reviewing the theories which have been formulated on the subject of catalysis, the author advances the view that catalysis is due to the formation of intermediate compounds ("catalides") as a result of residual affinity. This does not apply to cases where the intermediate compound is a salt, or to catalysis by solvents, finely divided (colloidal) metals, or organic ferments.

W. R. S.

**Whole Number Isotopes and Allied Phenomena.** F. H. LORING (*Chem. News*, 1920, 120, 73—77).—A theoretical paper in which the experimental evidence supporting the idea of whole number isotopes is given, together with the spectroscopic examin-

ation of isotopes. The photoelectric effect in its connexion with isotopes is discussed, as well as the cyclic evolution of elements and isotopes. A table is given in the paper indicating the percentage of higher mass isotopes of the commoner elements. The whole discussion tends to show that the whole number isotopes are a reality, and that the isotopic proportions may modify the electrical properties of the elements.

J. F. S.

**Deduction of the Chemical Constants of Polyatomic Gases from Planck's Theory of Probability.** LÉON SCHAMES (*Physikal. Zeitsch.*, 1920, **21**, 38—39).—A mathematical paper in which a method of deducing the chemical constants of tri- and tetra-atomic gases is deduced. The results are compared with those deduced by Sackur (A., 1913, ii, 128) and Tetrode (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1167).

J. F. S.

**Chemical Constants; Moment of Inertia of the Molecule and the Quantum Theory of Gases.** LÉON SCHAMES (*Physikal. Zeitsch.*, 1920, **21**, 39—42. Compare preceding abstract).—The chemical constant  $i_c$  and the moment of inertia  $P \cdot 10^{40} = \frac{3}{2} \frac{PQ}{E}$  have been calculated by means of the equations previously developed (*loc. cit.*) for oxygen, carbon monoxide, nitrogen, carbon dioxide, and water. The following values for the moment of inertia are obtained: oxygen, 31.2; carbon monoxide, 10.07; nitrogen, 9.91; carbon dioxide, 5.80; and water, 1.365. The results are compared with the values of other investigators, particularly those of Langen (A., 1919, ii, 183), and found to be in very good agreement.

J. F. S.

**A Cheap and Simple Microbalance.** J. H. SHAXBY (*Proc. Physical Soc. London*, 1919, **32**, 21).—A balance for loads from 5 mg. to 5 deg., depending on the depression of a stretched thread, is described.

J. R. P.

**Condensers.** FRITZ FRIEDRICHS (*Zeitsch. angew. Chem.*, 1920, **33**, 29—32).—A critical discussion of the various forms of laboratory condensers which have been described in literature from the time of Liebig onwards. As regards efficiency, the screw-shaped condensing tube, with five "threads" and provided with an internal cooling jacket, gives the best results. This form of condenser is more suitable for use as a reflux apparatus than is the spiral form.

W. P. S.

## Inorganic Chemistry.

**Oxidation of Sulphurous Acid by Ferric Salts.** JULIUS MEYER (*Ber.*, 1920, 53, [B], 77—78).—In Houben's recent method for the estimation of ferrous and ferric iron together in acid solutions, the assumption is made that when a ferric salt is reduced by sulphur dioxide the increased acidity corresponds with two-thirds of the acid in combination with the ferric iron, according to the equation  $2\text{FeCl}_3 + \text{SO}_2 + 2\text{H}_2\text{O} = \text{FeSO}_4 + \text{FeCl}_2 + 4\text{HCl}$  (this vol., ii, 56). It is now stated that the reduction of a ferric salt most probably proceeds in stages; thus, first, a red ferric ferrisulphite,  $\text{Fe}[\text{Fe}(\text{SO}_3)_3]_3$ , is formed, which slowly changes in the cold, more quickly on warming, into the ferrous salt, not, however, with the production of sulphuric acid, but dithionic acid, thus:  $\text{Fe}[\text{Fe}(\text{SO}_3)_3]_3 = \text{FeS}_2\text{O}_6 + \text{FeSO}_3$ . Before any increase in the acidity can take place, therefore, the dithionate must be decomposed, thus:  $\text{FeS}_2\text{O}_6 + \text{H}_2\text{O} = \text{FeSO}_4 + \text{H}_2\text{SO}_3$ , and it is not quite certain whether this is completed even by vigorous boiling. J. C. W.

**The Advantages of the Synthesis of Ammonia at Very High Pressures.** GEORGES CLAUDE (*Compt. rend.*, 1920, 170, 174—177. Compare this vol., ii, 30).—Whereas it is necessary by the German method, working at a pressure of 200 atmos., to pass the reacting gases over the catalyst a considerable number of times, with removal of the ammonia after each passage, it is only necessary to do this three times at a pressure of 1000 atmos. Other advantages of working at the higher pressure on an industrial scale are claimed. [See, further, *J. Soc. Chem. Ind.*, 1920, 187A.] W. G.

**Formation of Free Hydrogen in the Reversed Ammonia Flame.** FRIEDRICH C. G. MÜLLER (*Zeitsch. angew. Chem.*, 1920, 33, 24).—The author finds that the products of combustion of ammonia in oxygen contain hydrogen and nitrogen in the ratio 2:3 by volume. Since the result is unaltered by cooling the flame with cold water (Raschig, A., 1919, ii, 148), it cannot be due to dissociation of ammonia. On the other hand, Raschig's assumption that the equation  $2\text{NH}_3 + \text{O}_2 = \text{N}_2\text{H}_2 + 2\text{H}_2\text{O}$  represents the first stage of the reaction, followed by instantaneous dissociation of  $\text{N}_2\text{H}_2$  and partial combustion of the hydrogen, does not account for the constancy of the proportion of hydrogen produced. J. K.

**The Velocity of Oxidation of Nitric Oxide.** EUGÈNE WOURTZEL (*Compt. rend.*, 1920, 170, 229—231).—The oxidation of nitric oxide takes place according to the equation of a reaction of the third order, thus:  $-dp_{\text{NO}}/dt = k(p_{\text{NO}})^2 p_{\text{O}_2}$ .

The action does not undergo any marked modification when half the nitric oxide is oxidised; consequently, the exclusive and rapid

formation of nitrites or of nitrosyl sulphate observed, when the gaseous products formed at the commencement of the reaction are treated with alkali or sulphuric acid, must be due to particular conditions of absorption and not of oxidation of the nitric oxide. Nitrogen trioxide, the formation of which has previously been proved (compare next abstract), is an ulterior product of the action and not its intermediate product. The velocity of this oxidation diminishes with rise in temperature.

W. G.

**The Existence of Nitrogen Trioxide in the Gaseous State.** EUGÈNE WOURTZEL (*Compt. rend.*, 1920, 170, 109—111. Compare this vol., ii, 108).—By measuring the contraction produced when known quantities of nitric oxide and oxygen are mixed, the nitric oxide being in excess, the authors have shown that under a total pressure of about one-quarter of an atmosphere an almost stoichiometric mixture of nitric oxide and nitrogen peroxide contains about 2.5% of nitrogen trioxide.

W. G.

**Direct Formation of Carbon Monoxide by Burning Carbon in Pure Oxygen.** FRIEDRICH C. G. MÜLLER (*Zeitsch. angew. Chem.*, 1920, 33, 36).—If pure oxygen is passed downwards through a vertical quartz tube, 25 cm. in length and not more than 13 mm. in diameter, filled with pieces of wood charcoal of the size of linseed, the gas leaving the lower end of the tube will contain 85% of carbon monoxide. The upper part of the charcoal must be heated by a burner before the oxygen is admitted, and it is essential that the combustion is allowed to proceed under reduced pressure. This is attained by connecting the lower end of the tube with a vessel filled with water and opening the tap of the oxygen reservoir so that water flows from the lower vessel at the rate of 2 litres per minute.

W. P. S.

**A Reaction of Potassium Anhydrotellurate.** P. HULOT (*Bull. Soc. chim.*, 1920, [iv], 27, 33).—If tellurous acid or alkali tellurites are brought to complete fusion with potassium nitrate, and the mass after cooling is extracted with water, potassium anhydrotellurate,  $K_2Te_4O_{13}$ , is left behind as a powder, which is insoluble in water or acids. If this powder is suspended in dilute hydrochloric acid and a few pieces of zinc are added, the salt gradually disappears and a black pulverulent powder, which is pure tellurium, is left behind.

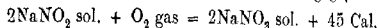
W. G.

**Application of the Reduction of Potassium Anhydrotellurate by Zinc to the Treatment of Tetradymite and to the Estimation of Tellurium in this Mineral.** PIERRE HULOT (*Bull. Soc. chim.*, 1920, [iv], 27, 100—101. Compare preceding abstract).—The tetradymite is first treated with dilute hydrochloric acid to remove the calcareous gangue. The powdered material is then dissolved in hot concentrated nitric acid, the solution being evaporated to dryness and the residue fused with twice its weight of potassium nitrate. The resulting mass contains potassium

sulphate and selenate, bismuth oxide, and potassium anhydrotellurate. The sulphate and selenate are removed with boiling water, and the residue is digested with dilute hydrochloric acid, whereby the bismuth oxide is dissolved out. The residue, after washing with dilute hydrochloric acid, is suspended in the same acid and some zinc is added. The whole of the tellurium is deposited in a pure state, and may be collected, dried, and weighed after the whole of the zinc has dissolved.

W. G.

**Reversible Oxidation of Sodium Nitrite.** C. MATIGNON and E. MONNET (*Compt. rend.*, 1920, **170**, 180—182).—Sodium nitrite, when heated in an atmosphere of oxygen at a pressure of 175 atmos. and at a temperature gradually rising from 395° to 530° during nine hours, is almost completely oxidised to sodium nitrate, the heat of formation of the nitrate being given by

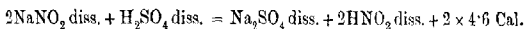


The reaction is too slow to be of practical use.

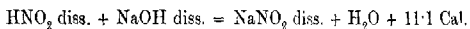
Calcium nitrite may similarly be converted into calcium nitrate.

W. G.

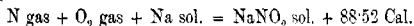
**Some Properties of Sodium Nitrite.** C. MATIGNON and (MILÉ.) G. MARCHAL (*Compt. rend.*, 1920, **170**, 232—233).—The authors find for the m. p. of sodium nitrite 276.9° (corr.). Its heat of solution is expressed by  $\text{NaNO}_2 \text{ sol.} + \text{Aq} = \text{NaNO}_2 \text{ diss.} - 3.52 \text{ Cal.}$  Its heat of decomposition in aqueous solution by dilute sulphuric acid is given by



From this equation and known data they deduce



and



Nitrous acid resembles nitric acid in its behaviour towards the following indicators: phenolphthalein, cochineal, litmus, *p*-nitrophenol, brazilin, and iodococsin, but decomposes others, like helianthin.

Aqueous sodium nitrite is not oxidised at 100° by prolonged contact with oxygen under a pressure of 50—55 atmos., even in the presence of a catalyst.

W. G.

**Ammonium Silicate. III.** ROBERT SCHWARZ and RICHARD SOUARD (*Ber.*, 1920, **53**, [B], 1—17. Compare A., 1917, ii, 31; 1919, ii, 283).—The authors have studied the electrical conductivities of solutions of dioxodisiloxane, monosilane, and silicic acid obtained from pure and technical sodium silicate, silicon tetrachloride, and tetrafluoride in ammonia, in order to determine whether there are any indications of the existence of ammonium silicate or of different molecular complexity in silicic acid of various origins. The increment of the conductivity of ammonia solutions suggests that salt formation does take place, just as the lowering



of the conductivity of sodium hydroxide by silicic acid points to the same conclusion. The dialysis of the preparations and the technique of the measurements are described.

It was soon found that the percentage of water in the preparation had a great influence on the conductivity, partly due to the different rates at which the silicic acid entered real solution. In order to eliminate this factor, or to follow it more closely, the solutions were filtered through an ultra-filter after determining the conductivity, and the amount of silica estimated. The quotient, increment of conductivity/dissolved  $\text{SiO}_2$ ,  $\Delta k/m=Q$ , therefore affords a clue to the molecular complexity of the silicic acid. The experiments show that a decrease in the proportion of water in the dioxodisiloxane or silicic acid preparation is accompanied by a fall in the value  $Q$ , not, however, gradually, but apparently in three stages. In the case of dioxodisiloxane, the value  $Q$  is about 75 when the material contains about 4.5% of water, about 50 if the proportion of water is 2%, even though the silicic acid may imbibe more water on keeping, and about 25 if the preparation is almost dry. Similarly with the various silicic acid preparations; no matter what their origin, the nearly dry specimens give a value of about 25, and those rich in water about 75. After ignition, however, silica causes no increment in the conductivity of ammonia solutions. The different values of  $Q$  suggest, therefore, that the dissolved silicic acid exists in three forms, of molecular weights in the ratio 1:2:3. The simplest forms are derived from dioxodisiloxane or monosilane, the direct hydrolysis of the latter in ammonia solutions being the most satisfactory way of preparing ammonium silicate solutions. J. C. W.

**Silver Peroxide and the Valency of Silver.** H. C. P. WEBER (*Trans. Amer. Electrochem. Soc.*, 1917, **32**, 391—404).—A number of experiments are described which were designed for the preparation of salts of silver in which the metal has a valency greater than unity. Except in the case of the peroxy-nitrate, the results were negative. This compound,  $2\text{Ag}_2\text{O}_2 \cdot \text{AgNO}_3$ , is formed on the anode during the electrolysis of silver nitrate, but if 15—25% of nitric acid is added to the solution there is no deposit, but a brown solution is formed. This solution, on examination, is found to contain both negative and positive silver-containing ions. The valency of the silver in the oxide portion of this salt is discussed. Two formulæ are put forward for the oxide part of the salt,  $\text{Ag}_2\text{AgO}_2$  (analogous to red lead) or  $\text{Ag}(\text{AgO})_2$  (analogous to magnetic iron oxide). The transference experiments show that one-third of the silver is cathodic and bivalent and two-thirds anodic and trivalent, which leads to the formula  $\text{Ag}(\text{AgO}_2)_2$ . This indicates that the oxide portion of the peroxy-nitrate is the silver salt of an unstable *argentic acid*,  $\text{HAgO}_2$ . J. F. S.

**Lead Borates.** H. V. THOMPSON (*Trans. Engl. Ceram. Soc.* 1918—1919, **18**, 510—511).—The white precipitate formed by mix-

ing cold concentrated solutions of lead nitrate and borax is of indefinite composition, and does not necessarily consist of lead metaborate,  $\text{Pb}(\text{BO}_2)_2 \cdot \text{H}_2\text{O}$ , as stated by Rose (*Ann. Phys. Chem.*, 1833, **29**, 455). The precipitate formed by adding an excess of a solution of borax to a solution of a lead salt consists of lead metaborate, and not the polyborate,  $2\text{PbO} \cdot 3\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ , as stated by Soubeiran (*J. Pharm. Chim.*, 1825, **11**, 31).

On boiling the metaborate with an excess of boric acid solution, no definite chemical compound is formed, in contradiction to Abegg ("Handb. anorg. Chem.," 1909, **3**, ii), who states that the compound  $\text{PbO} \cdot 2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  is produced.

The author confirms a statement by Le Chatelier (*Bull. Soc. chim.*, 1899, [iii], **21**, 35) that the compound  $\text{PbO} \cdot 3\text{B}_2\text{O}_3$  is formed on fusing boric acid and lead carbonate and extracting the mass with water to remove boric acid. [See also *J. Soc. Chem. Ind.* 1920, March.]

A. B. S.

#### Behaviour of Cerium Carbide towards Nitrogen. FR.

FICHTER and CHR. SCHÖLLY (*Helv. Chim. Acta*, 1920, **3**, 164—172).

—The requisite finely divided cerium carbide is prepared by heating a mixture of cerium dioxide (1 mol.) and carbon (6 atoms) in a graphite tube in an electric vacuum-oven at 1600°. It is found that this material, in spite of its apparent similarity to calcium carbide, does not yield any compound with nitrogen at 1250° which contains both carbon and nitrogen, but that the carbon is replaced by nitrogen, with the formation of cerium nitride. The possibility of the formation of cyanides and cyanamides from carbides appears to exist solely in the groups of the alkali and alkaline earth metals, and not in that of the earthy metals; it does not depend on the type of the carbide, but on the nature of the metal. Cerium carbide also reacts with ammonia at 1250°, yielding the nitride, but the action is slower and less complete than when nitrogen is used.

H. W.

#### Some Complex Compounds of Mineral Chemistry. G.

URBAIN (*Bull. Soc. chim.*, 1920, [iv], **27**, 81—94).—A lecture delivered before the French Chemical Society.

W. G.

#### Constitution of Ultramarine. LAURENZ BOCK (*Zeitsch.*

*angew. Chem.*, 1920, **33**, 23—24. Compare A., 1915, ii, 460; 1917, ii, 475).—Experiments on the action of ammoniacal silver chloride solution on artificial ultramarines are described. It is concluded that the blue rich in silica and sulphur, and based on the formula  $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ , is a definite chemical compound containing sodium, sulphur, aluminium, and silica in definite proportions; the same is true of the blue poor in silica but rich in sulphur. Further, the ultramarines are analogously constituted to the aluminium silicates. A table is given showing the known ultramarines and their relationship to natural and artificial silicates.

J. K.

**Equilibrium in Blast Furnace Reactions.** ERNST TERRES and AUREL PONGRACZ (*Zeitsch. Elektrochem.*, 1919, 25, 386—407).—The equilibrium of the reaction  $\text{Fe} + \text{CO}_2 \rightleftharpoons \text{FeO} + \text{CO}$  has been studied by a number of different observers, whose results show considerable divergencies. A fresh investigation has therefore been made on rather different experimental lines from those used hitherto. The reaction was studied from both sides, starting on the one hand from pure iron (iron wire or ferrum limatum) and carbon dioxide, and on the other from oxidised iron (prepared by oxidising pure iron with carbon dioxide) and carbon monoxide. The reaction was carried out in a pear-shaped glass vessel, which could be heated to any desired temperature in an electric furnace. For a full description of the special apparatus used, which embodied many devices for convenience and greater accuracy, the original must be consulted.

The usual procedure in studying such reactions as the one under consideration is to allow the reacting substances to remain in contact at the particular temperature until equilibrium is reached, and then to analyse the products. This method was used by Baur and Glaessner (*A.*, 1903, ii, 423), who plotted the composition of the gases at the end of the reaction against the temperature and obtained two distinct curves, the one obtained from the starting materials, iron and carbon dioxide, having a well-marked minimum, and the other, from ferrous-ferric oxide and carbon monoxide, showing an equally prominent maximum. The present authors allowed the reaction to proceed for a definite time at each particular temperature, and at the end of this time the gases were analysed. The reaction was studied over the temperature range 550° to 950°. The results are plotted in the form of four curves, two showing the composition of the gas mixture after seven hours, starting from either side of the equation, the other two after sixteen hours. Each curve is a straight line, the proportion of carbon monoxide in the mixed gases increasing steadily with the temperature. All four curves converge towards a point at about 950° with about 75% of carbon monoxide, showing that in seven hours equilibrium is already attained at this temperature. The two sixteen-hour curves lie between the seven-hour curves, quite close together, and converge at about 810°, showing that at this temperature equilibrium is reached in sixteen hours. The true equilibrium curve evidently lies about midway between the two sixteen-hour curves. Contrary to the results of Baur and Glaessner, the same equilibrium point is reached from either side of the equation, and the curve shows no maximum or minimum. These results are in agreement with those obtained by Schenck and his co-workers (*A.*, 1903, ii, 423; 1905, ii, 526; 1907, ii, 470) and by Levin (*A.*, 1912, ii, 1176).

Very careful experiments showed that the composition of the gas phase at equilibrium depends on the quantity of the solid phase present, the proportion of carbon monoxide increasing with increasing amounts of iron. This can be explained on the assump-

tion that the ferrous oxide phase is a solid solution of two components. A method for analysing the solid phase was devised, and it was shown that this always contained ferric iron. The proportion of ferrous to ferric oxide never corresponded with the composition  $\text{Fe}_3\text{O}_4$ . It was also shown that no other constituent was present in the solid phase. The fall in pressure always observed when carbon dioxide and iron are first heated together is due, not to any chemical reaction, but to absorption of the gas by the metal. [See also *J. Soc. Chem. Ind.*, 1920, 193A.] E. H. R.

**Behaviour of Iron in Contact with Sulphuric Acid.** C. E. FAWSITT and A. A. PAIN (*J. Proc. Roy. Soc. N.S. Wales*, 1918, 52, 396—405).—Differences in electrochemical behaviour show that no real similarity exists between iron which is slowly dissolving in concentrated sulphuric acid and iron rendered "passive" by dipping into nitric acid. The slowing down or cessation of the reaction is due apparently to the formation of a form of ferrous sulphate monohydrate on the surface of the iron. Although, generally speaking, increased dilution of the acid with water results in greater reactivity, certain anomalies were observed in this respect, notably that 89.3% acid has considerably less solvent action than either weaker or stronger acid of 94%, 90.9%, 87.9%, or 85% strength. The solvent effect is in all cases noticeably increased by shaking the containing vessel. G. F. M.

**The Critical Points of Self-hardening Steels.** P. DEJEAN (*Compt. rend.*, 1919, 169, 1043—1045).—It has previously been shown (A., 1917, ii, 477) that there is a distinct discontinuity between the formation of perlite or troostite and martensite, the critical point corresponding with the formation of the former being "A" and of the latter "B." It is now noted from a study of the cooling curves of a nickel-chrome-copper steel, which, starting from different initial temperatures, was cooled from 700° to 100° in about one hundred and fifty minutes, that the formation of martensite apparently occurs in two stages denoted by critical points  $B_1$  and  $B_2$ . The point A is indicated only when the critical temperature of cooling is 790°. When this temperature rises to 800°, A is considerably suppressed and the critical point  $B_1$  appears at about 420°. If the steel is cooled from 850° the second point  $B_2$  occurs at about 230°, and if cooled from still higher temperatures  $B_1$  disappears and the point  $B_2$  exists alone. If only the point A is in evidence during cooling the steel is relatively soft, but becomes harder when  $B_1$  predominates and still harder when  $B_2$  appears. It is concluded that for the steel studied the maximum hardness is reached in at least two stages, and that for the same steel there may be several martensitic forms. W. G.

**The Formula of Chromium Hydroxide.** MIL. Z. JOVITSCHITSCH (*Helv. Chim. Acta*, 1920, 3, 46—49).—The solubility of chromium hydroxide in ammonia and the preparation from such solutions of complex salts which invariably contain  $10\text{H}_2\text{O}$  (compare

A., 1913, ii, 223) leads the author to assign the formula  $\text{Cr}_4(\text{OH})_3\text{O}_2 \cdot 10\text{H}_2\text{O}$  or  $\text{Cr}_4(\text{OH})_{10}\text{O}_9 \cdot 9\text{H}_2\text{O}$  to chromium hydroxide. Stronger evidence in favour of such formulation is found in the absorption of carbon dioxide from the air by chromium hydroxide with the formation of a carbonate,  $\text{CO}_3 \cdot 2\text{Cr}_2(\text{OH})_6 \cdot 8\text{H}_2\text{O}$ , to which the formula  $\text{Cr}_2(\text{OH})_5 \cdot \text{O} > \text{CO}_3 \cdot 9\text{H}_2\text{O}$  or  $\text{O} < \text{Cr}_2(\text{OH})_4 \cdot \text{O} > \text{CO}_3 \cdot 10\text{H}_2\text{O}$  is ascribed (compare A., 1914, ii, 373). H. W.

**Chromium Chromate,  $\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ .** MIL. Z. JOVITSCHITSCH (*Helv. Chim. Acta*, 1920, 3, 40—46).—When a solution of chromium oxide in nitric acid (compare A., 1912, ii, 261) is evaporated until excess of acid is removed and the residue is dissolved in water and treated with ammonia, a dark brown, almost black product is obtained, analyses of which are in agreement with the formula  $\text{Cr}_2(\text{OH})_8 \cdot \text{H}_2\text{O}$  or  $\text{CrO}_3 \cdot \text{Cr}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ . The loss of  $1\text{H}_2\text{O}$  over sulphuric acid, of  $2\text{H}_2\text{O}$  at  $105^\circ$ , and of  $6\text{H}_2\text{O}$  at  $205^\circ$  is more readily explained by the former, but the chromium content and particularly the possibility of the preparation of anhydrous chromium chromate from the substance, lead the author to give preference to the latter. The substance is somewhat unstable and loses chromium trioxide when repeatedly washed even with warm water. It forms a very suitable initial material for the preparation of pure chromium hydroxide free from alkali, which is effected by boiling a solution of the substance in concentrated hydrochloric acid with alcohol until reduction is complete and subsequently adding ammonia in excess.

Anhydrous chromium chromate cannot be prepared by heating the hydrated product, since decomposition occurs before the last molecule of water is removed; it may, however, be obtained as a porous, black mass by dissolving chromium oxide in nitric acid, evaporating the solution to dryness, and cautiously heating the residue to  $290^\circ$ . The analytical data agree equally well with those required for the peroxide,  $\text{CrO}_2$ , but the readiness with which the substance is converted by ammonia, alkali carbonate, or hydroxide or by boiling water into chromium hydroxide and chromate is interpreted in favour of a salt-like constitution. H. W.

**Electro-deposition of Nickel.** L. D. HAMMOND (*Trans. Amer. Electrochem. Soc.*, 1916, 30, 103—134).—The best conditions for securing a satisfactory anode corrosion in the electro-deposition have been sought by studying the polarisation pressures and the current efficiency obtained with anodes of cast nickel, electrolytic nickel, and annealed nickel in solutions of nickel sulphate containing measured amounts of boric acid and nickel chloride. The experiments show that although cast nickel anodes corrode fairly well in simple sulphate solutions to which boric acid has been added, the best results are obtained when the purest electrolytic nickel in nickel sulphate solutions containing chloride is used. Nickel chloride is to be preferred to other chlorides, as its addition does

not decrease the concentration of nickel in the electrolyte. It is shown that 6 grams of nickel chloride per litre produce a good anode corrosion, and that the best results are secured by increasing the concentration of nickel chloride to 15 grams per litre. The conditions necessary for the direct electro-deposition of nickel on zinc have been investigated. It is shown that nickel can be directly deposited on zinc from the baths used to deposit nickel on more electro-negative metals if a higher initial current density is employed than is usual when using these baths for their ordinary purposes. An electrolyte consisting of 120 grams of nickel sulphate, 15 grams of nickel chloride, 30 grams of boric acid, and 1000 c.c. of water may be used to deposit nickel on zinc, copper, brass or iron. To deposit on copper a current density varying from a few tenths of an ampere to 3 or 4 amperes may be used, but to deposit on zinc a current density of not less than 3 amperes must be employed. It is suggested that whilst the above-named bath produces good deposits on flat strips of zinc, it will probably give a deposit with black streaks if irregular objects are to be plated. The following bath composition, however, produces perfect deposits on irregular objects: 240 grams of nickel sulphate, 15 grams of nickel chloride, 30 grams of boric acid, 175 grams of sodium citrate, and 1000 c.c. of water. This bath gives good deposits with current densities 0.5–7 amperes per sq. dm. if pure nickel anodes are used. The two baths named are very rapid in their action. Nickel has been deposited directly on zinc from a  $N/2$ -solution of hydrochloric acid containing 120 grams of nickel sulphate per litre. Sodium citrate has a beneficial effect on baths for the direct nickeling of zinc, which is not due to a change in the potential of zinc, but to a decrease in the rate of deposition by immersion. Sodium potassium tartrate and sodium malate have a similar action, but they do not permit the use of so high a current density as the citrate bath. The substitution of nickel ammonium sulphate by nickel sulphate in nickeling baths is recommended. To ensure a good deposit of nickel it is essential that the bath should be slightly acid, and it is for this purpose that boric acid is added. The function of the boric acid is therefore to maintain a small but fairly constant concentration of hydrogen ions in the electrolyte.

J. F. S.

#### **Isolation of Molybdenum and working up of Molybdenum**

**Residues.** S. MALOWAN (*Chem. Zeit.*, 1918, 42, 410).—To recover molybdic acid used as a precipitant in phosphorus determinations, the liquor is precipitated with sodium or calcium phosphate. The yellow precipitate, after being washed and dried, is heated with excess of concentrated sulphuric acid until solution is complete and the acid colourless. The cold liquid is poured into eight to ten times its volume of water, and the molybdenum precipitated with excess of ferrocyanide. The precipitate is collected after three hours, washed with dilute ferrocyanide solution until all the acid is removed, dried, separated from the paper, and ignited at a dark red heat to incipient fusion. The cooled product is leached

twice with hot water, then extracted with ammonia, which dissolves molybdic acid. The colourless solution is filtered, evaporated to dryness, the residue dissolved in a little water and hydrogen peroxide, and the solution boiled to oxidise any lower oxides. The resulting solution of ammonium molybdate is diluted until it has D<sub>17</sub> 1.09 (that is, 10 per cent.).

W. R. S.

**Reversible Reaction of Water on Molybdenum.** GEORGES CHAUDRON (*Compt. rend.*, 1920, 170, 182—185).—A study of the system water vapour-molybdenum-hydrogen-molybdenum dioxide over the temperature range 700—1100°. The values of  $K = p_{H_2O}/p_{H_2}$  obtained by the oxidation of the metal or the reduction of the oxide agree closely. Plotting  $\log K$  against  $1/T$ , the points obtained lie on a straight line within the temperature interval considered.

W. G.

**The Violet Compounds of Uranium.** J. ALOY and E. CHODIER (*Bull. Soc. chim.*, 1920, [iv], 27, 101—105).—The production of violet compounds of uranium as described by Aloy (compare A., 1901, ii, 317) is not an exceptional phenomenon, but quite general, and does not necessarily involve the action of light. It is necessary to distinguish between salts of inorganic acids and salts of organic acids. Salts of the first type must be used in exactly neutral solution and in the presence of a readily oxidisable substance. Both violet and ultra-violet rays cause the production of violet precipitates, the ultra-violet rays being the more active. The action of light is not always necessary, and it is shown that these violet compounds are obtained whenever a uranous and a uranic salt are present together at the requisite temperature in a neutral or feebly acid medium.

In reality, there exist a large number of violet compounds of uranium, having an analogous constitution, all of which, by loss of their acid radicles, tend to become transformed into the green, hydrated oxide,  $U_3O_8 \cdot 2H_2O$ .

W. G.

**Soluble Metastannic Acid.** HANS KREIS (*Schweiz. Chem. Zeit.*, 1919, 389).—Spongy tin is dissolved in a solution of ferric nitrate in nitric acid, D 1.23, and, after the vigorous reaction has subsided, hot water is added. The resulting, slightly opalescent solution contains colloidal metastannic acid, and may be repeatedly evaporated to dryness, with or without addition of more nitric acid, without precipitation of the tin (compare Antony and Mondolfo, A., 1899, ii, 330). The author considers that the ferric hydroxide formed by dissociation of the ferric nitrate acts as a protective colloid.

A. R. P.

**The Question of the Existence of Zirconium Monoxide.** R. SCHWARZ and H. DEISLER (*Ber.*, 1920, 53, [B], 1. Compare this vol., ii, 42).—A recognition of similar work by Wedekind (A., 1913, ii, 225).

J. C. W.

### Electrolysis of Aqueous Solutions of Vanadium Salts.

SIEGFRIED FISCHER, jun. (*Trans. Amer. Electrochem. Soc.*, 1916, **30**, 175—228).—Several hundred experiments are described in tabular form, which have been made with the object of depositing metallic vanadium from aqueous solutions. After a resumé of the literature of the deposition of vanadium, the author describes fifty-five experiments made with Cowper-Coles vanadium electrolyte (1.75 vanadium pentoxide, 2.00 sodium hydroxide, 160.0 water, and after boiling 32.0 hydrochloric acid) (A., 1899, ii, 755). It is found that in no circumstances can metallic vanadium be obtained from this electrolyte. The reduction of the electrolyte is limited in most cases to the vanadyl state, which is blue ( $V_2O_4$ ). A reduction occurs in practically all the experiments. At temperatures of  $90^\circ$  or above, the reduction may be taken to the sesquioxide ( $V_2O_3$ ), or green state, at temperatures below  $90^\circ$ ; above  $90^\circ$  the electrolyte is reduced to the lavender state. Carbon electrodes reduce the electrolyte to the green state. At temperatures below  $90^\circ$  platinum electrodes reduce the electrolyte to the blue vanadyl state only, and the current density has no influence on this. At temperatures above  $90^\circ$  the lavender state is reached only when porous cells are used. The black deposit obtained by Cowper-Coles on platinum electrodes is not a vanadium compound, but platinum hydride. A number of experiments (112) were made with solutions of vanadium pentoxide in sulphuric acid in the presence of various concentrations of aluminium sulphate, magnesium sulphate, ammonium sulphate, hydrofluoric acid, boric acid, or silicic acid, using electrodes of platinum, carbon, lead, and mercury. When platinum electrodes were used a black film was obtained, which contained no vanadium. In no case was metallic vanadium obtained. Solutions of vanadic acid in hydrochloric acid, sulphuric acid, nitric acid, hydrofluoric acid, lactic acid, ethyl hydrogen sulphate, and tartaric acid were electrolysed, as well as a series of solutions of vanadic oxide in alkali hydroxide, but in no case could metallic vanadium be obtained. The reason for the failure to obtain metallic vanadium is the very large heat of formation of vanadium salts. Thus the oxide  $V_2O_5$  has a heat of formation 441000 cal.;  $V_2O_3$ , 353200 cal.; VO, 104300 cal.

J. F. S.

### Formation and Nature of Black Antimony Trisulphide.

FERRUCCIO DE BACHO (*Annali Chim. Appl.*, 1919, **12**, 143—152).—On heating red antimony trisulphide in carbon dioxide, there is no material difference in the loss of weight at temperatures from  $150^\circ$  to  $300^\circ$ , the change to the black modification taking place at  $212^\circ$ , whilst in a current of hydrogen sulphide the change occurs at  $207^\circ$ . By adding ammonium chloride to the red sulphide, the temperature of the change in carbon dioxide is lowered (for example, to  $170^\circ$ ), whilst the presence of antimony chloride reduces the temperature still further. Thus in the case of a mixture of equal parts of antimony trisulphide and trichloride, the black



coloration appeared at 125°. Metallic silver also has a favourable influence on the transformation. The action of ammonium chloride in boiling solution also promotes the formation of the black sulphide to an extent depending on the concentration of the solution, whilst the rapidity of the transformation stands in relationship to the degree of hydrolysis of the ammonium chloride, and consequent acidity of the solution. The presence of antimony trichloride facilitates this conversion, which is accelerated by the presence of hydrochloric acid, antimony trisulphide, and potassium nitrate at high concentrations. Concentrated solutions of electrolytes, such as sodium chloride, ammonium sulphate, or potassium nitrate alone have no effect on the transformation, which is therefore not merely the result of molecular condensation. The conversion always takes place when the conditions permit of immediate contact between the red antimony trisulphide and antimony trichloride, whether added as such or formed in the solution. It is probable that the following reaction takes place:  $2\text{Sb}_2\text{S}_3 + 2\text{SbCl}_3 \rightarrow 6\text{Sb} + 3\text{S}_2\text{Cl}_2$ . It is also probable that the trace of free antimony thus formed, or that produced by dissociation of the red trisulphide when heated, forms in the colloidal condition a solid solution with the antimony trisulphide. This decomposition, which occurs in the process of drying in analytical work, is too small to be detected gravimetrically. On heating the red trisulphide, there is a gradual increase in the specific gravity, but the conversion into the black modification is not indicated by any sudden rise in the specific gravity.

C. A. M.

**The Action of Aqua Regia on Gold-Silver Alloys in the Presence of Ammonium Salts.** WILLIAM BRANCH POLLARD (T., 1920, 117, 99—103).

## Mineralogical Chemistry.

**Colloid Colour Substances in Minerals.** C. DOELTER (*Kolloid Zeitsch.*, 1920, 26, 23—27).—A theoretical paper in which it is shown that the colours of many minerals are due to small quantities of impurities, which may be the same in differently coloured minerals. The nature of the colour depends on the size of the particles of the pigment. Change in the colour effected by heating or by the action of radium rays is due to a change in the dimensions of the particles.

J. F. S.

**A Markedly Ceritic Fluorapatite from Latium.** I. BELLUCCI and L. GRASSI (*Gazzetta*, 1919, 49, ii, 232—246).—A nodule included in the building stone known as "peperino," occurring in a cave in the Ariccia district, is found to consist principally of olivine and biotite, together with numerous small, shining, crystalline aggregates having a radiating, fibrous structure and a pale emerald-green colour. This green mineral, D 323—329,

n 1.63—1.65, is a fluoapatite containing comparatively large proportions of rare earths; analysis gave:

CaO.	Rare earth oxides.	FeO.	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	F.	Total.
50.86	5.24	1.92	35.5	2.59	3.37	99.48

The rare earths present are ceritic and not yttric in character, the presence of cerium, didymium, and lanthanum being demonstrated.

A summary is given of the literature dealing with apatites containing rare earths. In the apatite of Narsarsuk, Flink (A., 1900, ii, 410) found 3.36% of yttric oxides and 1.52% of ceritic oxides.

T. H. P.

### The Origin of the Beds of Sodium Carbonate in Peru.

ERM. POZZI-ESCOT (*Bull. Soc. chim.*, 1919, [iv], 25, 614—617).—It is suggested that the sodium sulphate of the soil dissolves in the water which gradually collects in natural depressions, forming salt marshes, with an abundance of vegetation suited to the conditions. The sulphate in contact with the plants and algae becomes reduced to sulphide, which is then in its turn decomposed by carbon dioxide, either atmospheric or that resulting from local vegetative combustion, with the resulting formation of sodium carbonate or sodium hydrogen carbonate. The industrial possibilities of these deposits are discussed.

W. G.

**Mineralogy of Sweden.** GUST. FLINK (*Arkiv Kemi Min. Geol.*, 1917, 6, No. 21, 1—149).—In Part IV of his "Mineralogy of Sweden," the author gives detailed descriptions of forty-five

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	PbO.	GIO.
I.....	16.61	—	—	—	77.63	—
II.....	16.50	—	—	—	77.70	—
III.....	17.74	—	—	—	66.53	—
IV.....	17.21	—	—	—	70.14	—
V.....	39.84	—	—	0.15	—	16.53
VI.....	40.00	—	—	trace	—	11.49
VII.....	37.53	23.79	7.73	3.85	—	—
VIII.....	45.53	23.07	1.93	—	—	—
IX.....	43.54	22.62	1.79	—	—	—
X.....	43.40	23.05	1.27	—	—	—
	MnO.	CaO.	MgO.	H <sub>2</sub> O.	Total.	Sp. gr.
I.....	0.35	1.75	0.41	0.40	99.95*	6.53
II.....	2.83	0.52	0.10	0.08	99.82†	6.706
III.....	2.88	10.42	0.45	0.60	99.11‡	5.576
IV.....	2.78	7.31	0.95	—	98.39§	—
V.....	26.82	15.67	0.55	0.54	100.10	3.404
VI.....	7.05	37.82	0.94	2.48	99.93	3.16
VII.....	0.48	21.97	0.34	3.14	99.63**	3.189
VIII.....	—	25.48	—	4.48	100.49	—
IX.....	—	26.56	—	4.81	99.32	2.914
X.....	trace	26.49	0.40	4.89	99.50	2.906

\* Including Fe 0.10, Cl trace.

† Including ZnO 0.90, K<sub>2</sub>O 0.09, Na<sub>2</sub>O 0.40, SO<sub>3</sub> 0.63, Cl 0.12.

‡ Including Na<sub>2</sub>O 0.06, K<sub>2</sub>O 0.17, CO<sub>2</sub> 0.26.

§ Including Cl 0.10.

|| Including F 0.15.

\*\* Including TiO<sub>2</sub> 0.11, K<sub>2</sub>O 0.24, Na<sub>2</sub>O 0.45.

species belonging to the silicate group. Analyses are given of the following: I and II, barysilite of different types from Jakobsberg; formula,  $\text{Pb}_3\text{Si}_2\text{O}_7$ . Ganomalite, III, from Jakobsberg, IV from Långban. V, trimerite from Jakobsberg; formula,  $\text{Gl}_2\text{SiO}_4(\text{Mn,Ca})_2\text{SiO}_4$ . VI, harstigte from Harstig mine; formula,  $\text{Gl}_2\text{Ca}_2\text{Si}_3\text{O}_{11}$ . VII, epidote from Nols felspar quarry, Göta. Prehnite, VIII from Uppsala district, IX from Hästberg estate, near Falun, X from Sjösa iron mine, near Svärta.

L. J. S.

#### Presence of Lithium in the Salts of Vesuvian Fumaroles.

L. DE LUISE (*Gazzetta*, 1919, **49**, ii, 328—329).—The salts from the fumaroles of the crater of Vesuvius have the composition: potassium chloride, 20.521%; sodium chloride, 79.458%; iron and aluminium, traces. Sometimes lithium is present in small proportion, and in one instance 180 grams of the mixed chlorides were found to contain lithium chloride corresponding with 0.07 gram of lithium sulphate.

T. H. P.

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### Analytical Chemistry.

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#### Qualitative Analysis in the Presence of Phosphoric Acid.

HEINRICH REMY (*Zeitsch. anal. Chem.*, 1919, **58**, 385—392).—The following procedure is recommended for the qualitative analysis of a solution containing various metals, etc., and phosphoric acid. Heavy metals are first separated by means of hydrogen sulphide; the filtrate from the sulphide precipitate is boiled to expel hydrogen sulphide, filtered, heated with the addition of a small quantity of nitric acid, then nearly neutralised with ammonium carbonate, treated with an equal volume of concentrated ammonia, and an excess of ammonium phosphate is added. Aluminium, chromium, iron, calcium, strontium, barium, manganese, and magnesium are precipitated, whilst zinc, nickel, cobalt, and alkali metals remain in solution. The precipitate is dissolved in warm dilute hydrochloric acid, potassium sulphate solution is added, and the precipitated alkali earth sulphates are collected on a filter and separated and identified in the usual way. The filtrate from the sulphates is boiled with the addition of sodium acetate and ammonium chloride; iron, chromium, manganese, and aluminium are precipitated, whilst magnesium and a small quantity of calcium remain in solution. The precipitate is dissolved in hydrochloric acid, boiled, nearly neutralised with sodium carbonate, and then poured into a mixture of hydrogen peroxide and 20% sodium hydroxide solution. Iron and manganese are precipitated, whilst chromium and aluminium are converted into soluble chromate and aluminate respectively. The filtrate from the first phosphate precipitate, and

containing the zinc, etc., is heated, treated with ammonium sulphide, the precipitate is collected (the filtrate from this precipitate contains the alkali metals), and the zinc sulphide is dissolved in dilute hydrochloric acid, in which nickel sulphide and cobalt sulphide are insoluble. The hydrochloric acid solution is then rendered strongly alkaline with sodium hydroxide, heated, diluted, and filtered; zinc is precipitated from the filtrate as sulphide after the addition of acetic acid. Nickel and cobalt are separated and identified in the usual way.

W. P. S.

**Method of Stating Analytical Results.** A. THIEL (*Chem. Zeit.*, 1920, **44**, 81—82).—A discussion advocating the use of equivalent units in expressing the results of analysis. W. P. S.

**Influence of Temperature on the Strength of Standard Solutions in Quantitative Analysis.** YUKICHI OSAKA (*J. Tokyo Chem. Soc.*, 1919, **40**, 424—449).—The tables previously published (*ibid.*, 1911, **32**, 450) showing the changes in the concentration of standard solutions at different temperatures, taking 15° as the standard temperature, have been extended for temperatures from 5° to 30°, each being compared with three standards, at 15°, 20°, and 25°. Nineteen tables are given for *N*- and *N*/10-oxalic acid, *N*-hydrochloric, nitric, and sulphuric acids, *N*- and *N*/10-sodium carbonate, *N*/10-sodium hydroxide, *N*/10- and *N*/100-sodium chloride, *N*/10- and *N*/100-silver nitrate, *N*/10- and *N*/100-potassium permanganate, *N*/10-ammonium thiocyanate, and water. The change in the concentration of the solution and in the volume of the flask produced at different temperatures is recorded. The results are summarised in the following table:—

Standard temp. :	15°.		20°.		25°.	
Solution temp. :	5°.	30°.	5°.	30°.	5°.	30°.
NaOH ( <i>N</i> ) .....	1.00245	0.99508	1.00393	0.99655	1.00559	0.99819
Na <sub>2</sub> CO <sub>3</sub> ( <i>N</i> ) .....	1.00230	0.99321	1.00374	0.99664	1.00534	0.99820
HNO <sub>3</sub> ( <i>N</i> ) .....	1.00227	0.99316	1.00371	0.99658	1.00534	0.99820
H <sub>2</sub> SO <sub>4</sub> ( <i>N</i> ) .....	1.00231	0.99316	1.00365	0.99659	1.00526	0.99813
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ( <i>N</i> ) .....	1.00160	0.99580	1.00279	0.99668	1.00422	0.99840
HCl ( <i>N</i> ) .....	1.00153	0.99608	1.00264	0.99718	1.00395	0.99849
NaCl (0.1 <i>N</i> ) .....	1.00108	0.99642	1.00201	0.99735	1.00321	0.99854
AgNO <sub>3</sub> (0.1 <i>N</i> ) .....	1.00105	0.99640	1.00202	0.99737	1.00321	0.99856
NH <sub>4</sub> CNS (0.1 <i>N</i> ) .....	1.00104	0.99639	1.00199	0.99734	1.00322	0.99856
KMnO <sub>4</sub> (0.1 <i>N</i> ) .....	1.00096	0.99643	1.00193	0.99737	1.00312	0.99856
Na <sub>2</sub> CO <sub>3</sub> (0.1 <i>N</i> ) .....	1.00095	0.99675	1.00177	0.99757	1.00287	0.99866
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (0.1 <i>N</i> ) .....	1.00078	0.99674	1.00161	0.99757	1.00270	0.99866
NaCl (0.01 <i>N</i> ) .....	1.00089	0.99649	1.00178	0.99738	1.00235	0.99853
AgNO <sub>3</sub> (0.01 <i>N</i> ) .....	1.00089	0.99655	1.00177	0.99743	1.00234	0.99858
KMnO <sub>4</sub> (0.01 <i>N</i> ) .....	1.00087	0.99653	1.00181	0.99745	1.00234	0.99858
H <sub>2</sub> O .....	1.00083	0.99661	1.00174	0.99751	1.00238	0.99864

The average from all equinormal solutions is given in the final table for each temperature from 5° to 30° against three standard temperatures. This table could be used for any *N*-solution, within error of 5 in 10,000. Another table is given which could be applied for any solution less than 0.1*N* within error of 5 in 10,000. It is

pointed out that maximal errors for two solutions of equal strength made at two extreme temperatures ( $5^{\circ}$  and  $30^{\circ}$ ) is 7:1000 for  $N$  and 5:1000 for solutions less than  $0.1N$ .

#### CHEMICAL ABSTRACTS.

#### The Effect of a Change in Temperature on the Colour Changes of Methyl-orange, and on the Accuracy of Titrations.

HENRY THOMAS TIZARD and JOHN REGINALD HARVEY WHISTON (T., 1920, 117, 150—156).

**Indicator Papers.** D. J. DE JONG (*Pharm. Weekblad*, 1919, 56, 465—467).—An extension and amplification of previous communications (*ibid.*, 179, 238, 328, 404, 405). If a drop of acid is placed on ordinary filter paper and tested with methyl-orange, a weak reaction will be indicated in a ring surrounding the drop, and beyond this will exist a neutral "water ring." If the paper is previously treated with hydrogen chloride, washed, and dried, it becomes saturated with hydrogen ions, and further absorption of these from the drop will be prevented. A stronger coloration will thus result, and will be produced in the whole moistened portion. Addition of acid to methylene-blue similarly increases its sensitiveness.

W. J. W.

**Use of the Electrometer for Titrations.** J. PINKHOFF (*Pharm. Weekblad*, 1919, 56, 1218—1234).—The author gives a description of the apparatus and mode of operation in carrying out titrations by the potential method. A difference of potential of 1 millivolt should be detected by a suitable electrometer. The scope of the method and its special applications are discussed at some length.

W. J. W.

**Use of Arsenious Anhydride in Namias' Method of Volumetric Analysis.** FERRUCCIO DE BACHO (*Annali Chim. Appl.*, 1919, 12, 136—142).—In Namias's method (A., 1892, 1374) any given oxidising agent is treated with an excess of arsenious anhydride in the presence of ammonium acetate, and the boiling liquid titrated with iodine solution after the addition of acetic acid. Critical experiments have shown that this method is untrustworthy. No blue coloration is given by starch paste with iodine at  $60$ — $70^{\circ}$ , and it is therefore useless to employ it as an indicator in a boiling solution. The presence of ammonium chloride formed from the ammonium acetate when the solution contained hydrochloric acid also influences the results. Equilibrium between the reacting substances is then only very slowly attained. Contrary to the assertion of Namias, the reaction between arsenious anhydride and chromic acid is only complete after prolonged action, and the results obtained are invariably too high and not concordant.

C. A. M.

**New Volumetric Reduction Method with Arsenious Anhydride.** FERRUCCIO DE BACHO (*Annali Chim. Appl.*, 1919, 12, 153—174).—An oxidising agent is treated with excess of arsenious

acid solution in the presence of hydrochloric acid, and the solution subsequently titrated with standard potassium bromate solution, methyl-orange being used as indicator. To prevent loss through volatilisation of arsenic chloride the proportion of hydrochloric acid must not exceed 12.8%, a distinct loss occurring when it reaches 15%. In many cases the reduction is complete at the ordinary temperature, but as a rule it is preferable to boil the liquid beneath a reflux condenser. The method gives good results in the analysis of permanganates, in the estimation of manganese dioxide in pyrolusite, and the analysis of chlorates and chromates, including lead chromate. In the case of mixtures of hypochlorites and chlorates the hydrochloric acid is reduced to 5% to retard the action of the chlorate during the estimation of the hypochlorites. The acid is then increased to 12% and the reduction effected at boiling point, when both chlorates and hypochlorites react, and the amount of the former is found by difference. [See, also, *J. Soc. Chem. Ind.*, 1920, March.]  
C. A. M.

**Improved Electro-analysis Apparatus.** J. L. JONES (*Trans. Amer. Electrochem. Soc.*, 1917, **32**, 329—334).—A description of a six- and a ten-unit electrically stirred electrolytic apparatus for the quantitative analysis of non-ferrous alloys. The electrodes and beakers are fixed; stirring is effected by revolving tungsten rods. Each electrolysis receives a separate current which may be varied between 0.5 and 6.0 amps. A switch and push-button before each unit enable the current and *E.M.F.* to be read at any moment.

J. F. S.

**Use of Lead as a Substitute for Platinum in Analysis.** CARL HÜTTER (*Zeitsch. angew. Chem.*, 1919, **32**, 380).—Platinum basins may be replaced by lead basins for certain quantitative estimations. Thus in the case of chrome iron ore the mineral may be heated with concentrated sulphuric acid in a lead basin on the water-bath, and any lead sulphate formed removed without interfering with the subsequent analysis. The method is suitable for the estimation of silicon, aluminium, potassium, and sodium, for which silica or silver basins cannot be used. Any alteration in the stage of oxidation is prevented by introducing a current of carbon dioxide through a porcelain tube inserted into a hole in the middle of the lead cover of the basin.

C. A. M.

**Catalytic Reduction of Organic Halogen Compounds.** M. BUSCH (*Zeitsch. angew. Chem.*, 1918, **31**, 232).—In the catalytic reduction of organic halogen compounds by means of palladium, hydrazine may be substituted with advantage for a current of purified hydrogen. 0.2 Gram of the organic compound is dissolved in 40—50 c.c. of alcohol; 2 grams of palladinised calcium carbonate, or barium sulphate, 2.5 c.c. of 50% potassium hydroxide, and 10 drops of hydrazine hydrate are added. The liquid is boiled under reflux for thirty minutes, after which the bulk of the alcohol

is expelled on the water-bath. The catalyst is filtered off, and the halogen determined in the filtrate after acidification with nitric acid.

W. R. S.

**Estimation of Organic Chlorine or Bromine by the Chromic Acid Method.** P. W. ROBERTSON (*Chem. News*, 1920, 120, 54).—To overcome minor difficulties encountered in the chromic acid method of estimating organic chlorine or bromine (T., 1915, 107, 902), the following modifications are suggested. A freshly prepared cold solution of sodium peroxide is used as absorbing medium instead of sodium hydroxide solution containing hydrogen peroxide. The chromic anhydride may be replaced by halogen-free potassium dichromate, and  $N/20$ -solutions of silver nitrate and ammonium thiocyanate are recommended instead of  $N/10$ -solutions. Finally, in the case of compounds, particularly liquids, which react explosively with the oxidising mixture, the best procedure is to cover the substance with a large amount of powdered dichromate and run the previously cooled sulphuric acid very rapidly into the reaction vessel through a wide funnel by means of a suction pump connected with the absorption tube. The reaction vessel is cooled in ice until the initial violence of the oxidation has moderated.

G. F. M.

**Iodometric Estimation of Chloric Acid.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, 56, 460—465).—The direct iodometric estimation of chlorate in a strongly acid medium gives high results owing to oxidation of hydrogen iodide by atmospheric oxygen. Rupp's method (A., 1918, ii, 125) is satisfactory. It is sufficient, however, to use hydrochloric acid to the extent of one and a-half times the volume of the chlorate solution, and only 100 c.c. of potassium iodide need be added. By using ferrous sulphate, still smaller quantities of reagents may be employed. The chlorate solution is boiled with 10 c.c. of 4*N*-hydrochloric acid and ferrous sulphate; 1 gram of potassium iodide is added at 50°, and the solution then titrated with slight heating towards the end.

W. J. W.

**Estimation of Iodide.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, 56, 1029—1035).—Estimations were made by several known methods with the same preparation of potassium iodide (0.098*N*) in each case. Winkler's method (*Zeitsch. anal. Chem.*, 1914, 53, 20) gives good results only in absence of bromide. The presence of bromide in small quantities does not affect the results in the case of those methods in which hydrogen iodide is oxidised to iodine and the latter estimated, for example, Volhard's, Vincent's (A., 1900, ii, 166), and Richard's (*Pharm. Weekblad*, 1903, 40, 157). In the last mentioned method, it is advisable to let the solution remain for two to three minutes after addition of the tartaric acid. Iodide may be estimated in presence of bromide by adding benzoic acid and potassium iodate, boiling until the iodine has disappeared, then adding potassium iodide and sulphuric acid, and titrating back with thiosulphate.

W. J. W.

**Estimation of Oxygen with Cuprammonium Compounds.**  
W. HAEHNEL and M. MUGDAN (*Zeitsch. angew. Chem.*, 1920, **33**, 35).—In the preparation of ammoniacal copper solution for the absorption of oxygen, the usual ammonium carbonate solution employed may, with advantage, be replaced by saturated ammonium chloride solution. The rate of absorption of oxygen is not affected, but the residual gas is free from carbon dioxide derived from the ammoniacal copper solution.

W. P. S.

**The Volumetric Estimation of Sulphates by Oxidation of Benzidine Sulphate with Potassium Permanganate.**  
P. L. HIBBARD (*Soil Sci.*, 1919, **8**, 61—65).—A modification of the method of Raiziss and Dubin (compare A., 1914, ii, 671), full details being given. It is shown that both temperature and volume are important factors, which should be kept constant. The solution for the precipitation of benzidine sulphate should be free from organic matter, iron, the heavy metals, nitrates, and phosphates, and should contain between 0.5 and 4.0 mg. of  $\text{SO}_4^{2-}$ . It is advisable to use an excess of standard permanganate solution, the oxidation flask being heated in a boiling-water bath for ten minutes. At the end of this time, a slight excess of standard oxalic acid solution is run in, and this is then titrated back with the permanganate solution.

W. G.

**Estimation of the Non-protein Nitrogen in Blood.**  
B. ALBERT (*Biochem. Zeitsch.*, 1918, **92**, 397—412).—A modification of the micro-method for estimating the non-protein nitrogen in blood. The blood or serum is freed from its protein by the addition of colloidal iron and 10% potassium sulphate. The filtrate is oxidised with "micro-sulphuric acid," consisting of 15 grams of nitrogen-free potassium sulphate, 5 grams of pure copper sulphate, 100 c.c. of distilled water, and 400 c.c. of pure concentrated sulphuric acid. The distillation is carried out in an apparatus described by the author. The distilled ammonia is received in  $N/200$ -sulphuric acid and estimated iodometrically.

S. S. Z.

**Estimation of Urea Nitrogen in Blood (and Urine).**  
B. ALBERT (*Biochem. Zeitsch.*, 1919, **93**, 82—89).—The Lesser-Siebeck micro-method for the estimation of urea nitrogen is considered a very suitable one. Some modifications are recommended.

S. S. Z.

**Estimation of Small Quantities of Arsenic.** W. VAN RIJN (*Pharm. Weekblad*, 1919, **56**, 1072—1083).—Various methods of estimation of small quantities of arsenic, as in urine, have been investigated. Separation of the arsenic from the material under test is accurately effected by several methods, as follows: (a) Treatment with potassium chlorate and hydrochloric acid (Fresenius and Babo); (b) absorption by ferric hydroxide (Lockemann and Paucke, A., 1911, ii, 720); (c) acidification of the sample with



sulphuric acid, addition of solution of bromine in potassium bromide, then ammonia and magnesia mixture; (d) treatment with ammonia and magnesia mixture, and addition of sodium phosphate (Berntrop). Bloemendaal's apparatus was used for obtaining the mirror; final estimation of this by comparison with a standard mirror was not accurate, and the titration method (Berntrop, A., 1906, ii, 706) was used. Quantities as small as 1 mg. of arsenic per litre were estimated. The estimations were also carried out with wallpapers, paint, and blind materials. W. J. W.

#### Precision Method for the Estimation of Gases in Metals.

H. M. RYDER (*Trans. Amer. Electrochem. Soc.*, 1918, **33**, 197—204).—The metal to be investigated is mounted as a thin ribbon or filament in an electric light bulb, which is connected to a Toeppler pump and exhausted. The temperature of the filament is then raised by an electric current, and the pump set working, so that the gases are continuously removed. The temperature is raised in steps of  $50^{\circ}$  up to the melting point, and the gases evolved at each temperature are measured and analysed. The bulb is water-cooled to prevent the evolution of gases by the glass on heating. Silicon steel was found to give off large volumes of gas at  $730^{\circ}$ . In the analysis, the water vapour and carbon dioxide are frozen out by means of liquid air, and the remaining gases removed. The carbon dioxide is then removed by substituting carbon dioxide snow for the liquid air. The volume of carbon dioxide is measured by reading the pressure existing in the apparatus by means of a MacLeod gauge. It is then pumped out, and the water vapour released into the vessel by removing the refrigerant. The pressure due to this is read by means of a mercury U-tube manometer with optical lever attachment. Oxygen is added to the residual gases, and the hydrogen, methane and carbon monoxide are burnt to carbon dioxide and water, which are estimated as before. Carbon monoxide is added to the residual gases, and serves, after combustion, to estimate the excess of oxygen and any which may have been there originally. Nitrogen is estimated by difference. J. F. S.

#### New Absorption Apparatus for Elementary Analysis.

FRITZ FRIEDRICH (*Zeitsch. angew. Chem.*, 1919, **32**, 388).—A compact form of absorption apparatus is described in which the carbon dioxide is absorbed by means of potassium hydroxide solution in a helical tube, which is fixed within the bend of a U-tube. The latter is charged with calcium chloride instead of soda-lime. The use of calcium chloride as a drying agent is preferable to that of sulphuric acid when it is a question of equilibrium being attained. The binary system  $\text{CaCl}_2\text{--H}_2\text{O}$ , in which the phases  $\text{CaCl}_2$ ,  $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$  occur, is univariant, and the tension therefore depends on the temperature, but not on the concentration, whereas the system  $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ , in which only two phases,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , are formed, is bivariant, and its tension depends on the concentration as well as on the temperature. The use of both drying

agents, as hitherto, is unsuitable, since the tension of sulphuric acid is lower than that of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ . The gas must therefore be moistened, not dried, in the calcium chloride tube following the sulphuric acid vessel, or the results for hydrogen will be too low; under these conditions, calcium chloride dihydrate must be used instead of anhydrous calcium chloride. It is therefore advisable to discard the sulphuric acid and replace it by 50% potassium hydroxide solution and calcium chloride.

C. A. M.

**Estimation of Combustible Matter in Silicate and Carbonate Rocks.** A. C. FIELDNER, W. A. SELVIG, and G. B. TAYLOR (*U.S. Bureau of Mines*, 1919, Tech. Paper 212).—The method described is a modification of that devised by Lissner (*Chem. Zeit.*, 1910, **34**, 37–38), involving digestion of the silicate material with hydrofluoric and hydrochloric acids, and combustion of the insoluble residue. Carbonate rocks are treated with dilute hydrochloric acid to remove calcium carbonate, etc., and the process is applied to the insoluble residue. [See, further, *J. Soc. Chem. Ind.*, 1920, 155A.]

W. E. F. P.

**The Estimation of Calcium and Magnesium in Different Saline Media.** E. CANALS (*Bull. Soc. chim.*, 1919, [iv], **25**, 655–658. Compare A., 1919, ii, 34, 477).—For the volumetric estimation of small quantities of magnesium it is recommended that the magnesium should first be precipitated as magnesium ammonium phosphate, and then one of two methods adopted.

(1) The precipitate is washed centrifugally with dilute ammonium hydroxide and then dissolved in just sufficient 5% hydrochloric acid, the phosphoric acid in the solution being estimated by titration with an uranium solution (1 c.c. = 0.5 mg.  $\text{P}_2\text{O}_5$ ), using cochineal as an indicator. The results are accurate to 0.2 gram of magnesium.

(2) The precipitate is washed with a saturated aqueous solution of sodium phosphate, and then dissolved in hydrochloric acid, the ammonia present being estimated colorimetrically by means of Nessler's reagent. The results are accurate to 0.01 gram of magnesium.

W. G.

**Spectroscopic Estimation of Small Amounts of Lead in Copper.** C. W. HILL and G. P. LUCKEY (*Trans. Amer. Electrochem. Soc.*, 1917, **32**, 335–343).—A method is described for the rapid estimation of small quantities of lead in copper. A known weight (0.1–1.0 gram) of the sample in the form of a shot is placed in a small cavity in the lower positive graphite electrode of a carbon arc, and a fixed or rotating negative electrode used above. The arc is struck, the light focussed on to the slit of a grating spectroscope, and the time required for the complete disappearance of the bright lead line ( $405.8\mu\mu$ ) from the spectrum, or for its reduction to a definite feeble intensity, is measured by means of a stop-watch. With careful adjustment of the arc, the times vary

regularly with the amount of copper used and with its percentage of lead. Thus 0.2 gram of copper containing 0.004% of lead required 14 secs., whilst 1.0 gram of copper containing 0.038% of lead required 227 secs. A series of experiments made with 0.4 gram samples show that the analyses are sufficiently accurate for use in a copper refinery.

J. F. S.

**Estimation of Mercury.** H. B. GORDON (*Analyst*, 1920, 45, 41—46).—For the estimation of small quantities of mercury, a coil of copper gauze is suspended in the solution, which has previously received the addition of a small amount of hydrochloric acid and of copper sulphate; the gauze is kept in motion by a motor, and, after a suitable time, is removed from the solution, washed, dried, and weighed. It is then heated in a current of hydrogen, cooled in the same gas, and re-weighed; the loss in weight is due to the volatilisation of the deposited mercury. The volatilised mercury may be collected in a constricted portion of the heating tube and identified by the iodine test. As little as 0.1 mg. of mercury may be detected by the method. Nitrates do not interfere, but antimony, arsenic, bismuth, and silver should not be present, as they are liable to cause error unless the copper gauze is heated at such a temperature that the mercury alone volatilises. [See, further, *J. Soc. Chem. Ind.*, 1920, March.]

W. P. S.

**Detection and Estimation of Very Small Quantities of Chromium in Minerals and Ores containing Silicates and Carbonates.** O. HACKL (*Chem. Zeit.*, 1920, 44, 63).—One gram of the mineral is fused with eight times its weight of a mixture of sodium carbonate and potassium carbonate, the fused mass is treated with water, a drop of alcohol is added, the mixture heated to reduce and precipitate any manganese compounds present, and the solution is filtered. The filtrate is evaporated, but not so far that alkali salts crystallise out, again filtered, and diluted to a definite volume, which should be from 20 to 50 c.c., according to the quantity of chromium present. The chromium is then estimated colorimetrically, using as a standard a potassium chromate solution containing 0.0511 gram of the salt and a small quantity of sodium carbonate per 200 c.c.; each c.c. of this solution is equivalent to 0.1 mg. of  $\text{Cr}_2\text{O}_3$ .

W. P. S.

**A Very Sensitive Reagent for Cobalt.** I. BELLUCCI (*Gazzetta*, 1919, 49, ii, 294—298).—One mg. of cobalt in solution may be detected colorimetrically in 1–2 litres of water by means of  $\alpha$ -nitroso- $\beta$ -naphthol, and in about 17 litres of water by means of  $\beta$ -nitroso- $\alpha$ -naphthol (compare Atack, A., 1915, ii, 652; Jones, A., 1918, ii, 410; Bellucci and Chiucini, this vol., ii, 54). One mg. of nickel in 4–5 litres of water may be detected by means of dimethylglyoxime.

T. H. P.

**The Theory of Colour Lakes.** C. BRENNER (*Helv. Chim. Acta*, 1920, 3, 90—103).—The author has endeavoured to base

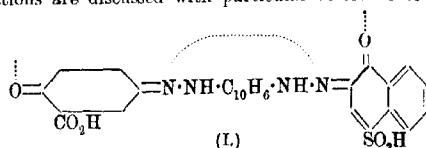
methods for the detection and estimation of minimal amounts of cobalt and copper on the colorations which the metallic ions give with nitrosonaphthols.  $\alpha$ -Nitroso- $\beta$ -naphthol is found to be unsuitable for this purpose in aqueous solution, since the lake is too easily precipitated, whilst chloroform or carbon disulphide solutions (in which cobalt "nitrosite" is readily soluble) are only adapted to the detection, but not to the estimation, of cobalt. On the other hand, the solubility of the lake in water can be sufficiently increased by introducing one or more sulphonic groups into the naphthol molecule. The colour of the lake depends on the number and position of the hydroxy- and sulphonic groups; the yellowest shade is given by the nitroso-derivative of "R"-acid, the deepest red with nitroso-1-naphthol-5-sulphonic acid, and the darkest shade with nitroso-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid (chromotropic acid). In ammoniacal solution, the latter gives a lake when metal and acid are in the proportion of 1 atom to 2 molecules, whilst in sodium hydroxide solution the requisite proportion is 1 : 6; attempts to base a colorimetric process for estimating cobalt on these data were unsuccessful, the results being 10—40% high. On the other hand, the acid can be used for the micro-titration of cobalt, since the yellow, ammoniacal solution of nitrochromotropic acid yields an immediate intense blue coloration with the cobalt ion, in the formation of which 2 molecules of the acid react with an atom of cobalt; when the cobalt ions have been completely converted into this compound, further addition of the acid causes a change in shade from blue to red. Test analyses show the method to be fairly accurate, but it cannot be used for cobalt in the presence of nickel, although the latter alone may also be estimated by the reagent. The micro-titration of copper can be effected similarly, but a larger excess of the reagent is required to give a definite end-point.

Other substances with properties similar to those of nitrochromotropic acid are found among azo-dyes which are used with metallic mordants, and among those which in dyeing are subjected to after-chroming. Thus, Diamond Black F gives a deep blue solution in aqueous alkali, which yields differently coloured lakes with ammoniacal solutions of the most various metals; when the metallic ion is completely united with the dye, addition of a further quantity of the latter causes a change in shade towards blue. The possible utility of the method is illustrated at the instance of copper.

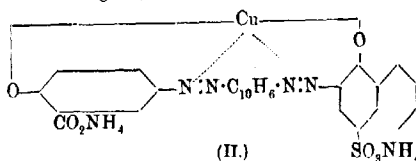
The possibilities of the formation of differently coloured complex compounds have been investigated for twenty different metals and sixteen dyes; such compounds appear to be formed most frequently with magnesium, the alkaline earth metals, and those of the iron group. It is interesting to note that chromium, which is so largely used in mordanting, is allied in this respect with the least reactive metals of the nitrogen family. The capability of the dye to form differently coloured complex compounds which are soluble in ammonia appears to depend on the presence of a hydroxyl group

in the ortho- or para-position to the azo-group, and, as a result of extensive experiments with a number of dyes, it is possible to give methods for the microchemical estimation of copper, silver, magnesium, zinc, cadmium, calcium, strontium, barium, iron, nickel, and cobalt.

The constitution of the lakes and the colour changes involved in the titrations are discussed with particular reference to Diamond



Black. In acid solution, the quinonoid formula (I) is ascribed to the dye in which two strong partial valencies are associated with the oxygen groups, whilst the other partial valencies of the azo-groups satisfy each other. The former valencies are



simultaneously, the partial valencies of the azo-groups are satisfied by those of the alkali metal. When, however, metallic ions are present in the solution, the subsidiary valencies of which are stronger than those of the alkali metals, the actual lake is produced, as indicated in formula (II). H. W.

**Estimation of Tungsten in Ferrotungsten.** Ludwig Löwy (*Zeitsch. angew. Chem.*, 1919, **32**, 379-380).—Ferrotungsten is completely decomposed when fused with ammonium sulphate and concentrated sulphuric acid, without the porcelain or platinum crucible being attacked, as when the fusion is effected with potassium hydrogen sulphate. The fused mass is dissolved in water, the solution treated with a little nitric acid, and then boiled with dilute (1:5) hydrochloric acid. The precipitated tungstic acid is separated and washed with dilute hydrochloric acid, the filtrate freed from iron by precipitation with ammonia, then acidified, and evaporated to dryness, the residue boiled with dilute hydrochloric acid, and the fresh precipitate of tungstic acid separated. For very accurate analyses, a third precipitation may be made. The united precipitates are ignited until constant in weight, evaporated with hydrofluoric acid, and again ignited and weighed. Any remaining iron may be separated by fusing the residue with sodium carbonate, extracting the mass with water, and weighing the residue of ferric oxide. [See, further, *J. Soc. Chem. Ind.*, 1920, 158a.] C. A. M.

**Estimation of Uranium and its Separation from Other Rare Elements.** C. A. PIERLÉ (*J. Ind. Eng. Chem.*, 1920, 12, 60—63).—It is shown that good results may be obtained by precipitating uranium with ammonium hydroxide, washing the precipitate with ammonium nitrate solution, and igniting it. Precipitation as uranyl ammonium phosphate by means of ammonium dihydrogen phosphate is also trustworthy, but has the drawback that the ignited uranyl pyrophosphate rapidly absorbs moisture. Precipitation as uranium sulphide and subsequent ignition invariably gives too high results, owing to part of the sulphur being oxidised to sulphate during the ignition. Volumetric estimation of uranium by means of potassium permanganate is inaccurate, owing to over-reduction taking place, and it is not possible to eliminate this or to continue the reduction to a definite point below the uranous condition. A method of separating uranium from vanadium, molybdenum, and tungsten has been based on Peligot's observation (*Ann. Chim. Phys.*, 1842, [iii], 5, 1) that uranyl nitrate is readily soluble in ether. The solution is evaporated to dryness, and the residue of uranyl nitrate, etc., is extracted with ether, in which vanadium pentoxide, molybdenum trioxide, and tungstic trioxide are insoluble. The dry residue should be moistened with nitric acid immediately before the extraction, and shortly after the process has begun, to reconvert into nitrate the partly decomposed uranyl nitrate. Another method of separating uranium from vanadium has been based on the fact that uranyl nitrate is readily soluble, whereas vanadium pentoxide is insoluble in acetic acid of 95% strength or above to which nitric acid has been added in the proportion of 1:20. The solution of uranyl nitrate and sodium metavanadate is evaporated to dryness with nitric acid, and the uranium extracted from the residue by means of the mixed acids. [See, further, *J. Soc. Chem. Ind.*, 1920, 209A.] C. A. M.

**Reaction of Tin Salts.** A. MAZUIR (*Ann. Chim. anal.*, 1919 [ii], 2, 9).—The reaction depends on the insolubility of stannous or stannic iodide in sulphuric acid. Two c.c. of the neutral or slightly alkaline solution containing the tin salt are treated with 2 c.c. of 10% potassium iodide solution and 1 to 2 c.c. of concentrated sulphuric acid. A yellow, crystalline precipitate of tin iodide forms at once if the solution under examination contains not less than 0.1 gram of tin per litre; the precipitate is soluble in chloroform, alcohol, and dilute hydrochloric acid. It is decomposed by ether, iodine being liberated. Arsenic gives a similar reaction, but the arsenic iodide formed is insoluble in dilute or concentrated hydrochloric acid. In the case of antimony, the iodide obtained is flocculent and brick-red in colour. W. P. S.

**Separation and Estimation of Lead and Bismuth.** G. LUFF (*Chem. Zeit.*, 1920, 44, 71).—A nitric acid solution of the two metals is neutralised with ammonia, saturated ammonium nitrite solution and sodium nitrite solution are added, the mixture is

diluted to about 200 c.c., and boiled. When the evolution of nitrogen ceases, the precipitate (bismuth hydroxide or basic bismuth nitrate) is collected on a filter, washed with hot water, then dissolved in nitric acid, the solution evaporated, and the residue ignited and weighed as  $\text{Bi}_2\text{O}_3$ . The filtrate is acidified with acetic acid, and the lead precipitated and weighed as lead chromate. The bismuth oxide, after weighing, should be treated with nitric acid and hydrofluoric acid, again ignited, and washed, to remove traces of silica and alkali respectively.

W. P. S.

#### **The Estimation of Acetylene in Gaseous Mixtures.**

J. A. MULLER (*Bull. Soc. chim.*, 1920, [iv], 27, 69--71).—The acetylene is absorbed in ammoniacal cuprous chloride, using a volume of gas containing at the most 10–11 c.c. of acetylene; the solution is acidified with acetic acid, and the cuprous acetyluride is collected and washed. The paper and precipitate are transferred to a platinum crucible, and sulphuric acid is added drop by drop until a homogeneous fluid mass is obtained. The excess of acid is gently evaporated, and when fuming has ceased, the crucible is heated to a red heat, cooled, and weighed.

W. G.

**Determination of the Composition of Mixtures of Alcohol and Water by Measurements of Electrical Conductivity.** I. M. KOLTHOFF (*Rec. trav. chim.*, 1920, 39, 126–134).—For the determination of the alcohol content of beer or wine, the following procedure is recommended. The excess of carbon dioxide is removed from the liquid by bubbling air through it, and the liquid is then distilled with magnesium oxide. Fifty c.c. of the distillate are mixed with 10 c.c. of approximately  $N/2$  oxalic acid solution, and the mixture is made up to 100 c.c. with water. The specific conductivities  $\sigma_1$  and  $\sigma_2$  of the mixture and of the original oxalic acid solution diluted to one-tenth with water are then determined. Then  $f_1 = 100 \times \sigma_1 / \sigma_2$ . This can then be corrected to  $f_{1s}$  by means of the temperature-coefficient, and a table is given showing the relationship between  $f_{1s}$  and the alcohol content of the distillate.

W. G.

**Specific Reaction of Butylene  $\beta$ -Glycol and of Acetylmethylcarbinol, Products of Butyleneglycollic Fermentation.** LEMOIGNE (*Compt. rend.*, 1920, 170, 131–132).—The characterisation of acetylmethylcarbinol in the products of microbic decomposition of sugars serves to differentiate certain groups of similar microbes, and the following method affords a ready means of detecting traces of this compound. The carbinol is oxidised to diacetyl by means of ferric chloride, the diacetyl being distilled off and detected by precipitation in ammoniacal solution as nickel dimethylglyoxime with a nickel salt and hydroxylamine. By this method it is possible to detect acetylmethylcarbinol at a dilution of 1 in 1,000,000. The reaction is not given by any other of the products of fermentation.

W. G.

**Microchemical Method of Estimating Dextrose. II.** IVAR BANG (*Biochem. Zeitsch.*, 1918, **92**, 344—347. Compare A., 1918, ii, 279).—It is found that the potassium iodate employed by the author in his modified method for the micro-estimation of sugar in blood does not keep well. He therefore uses free iodic acid instead. The solution is prepared by dissolving 0.3567 gram of pure potassium iodate in 10 c.c. of 20% sulphuric acid. 2.5 Grams of copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) may also be added to it at the same time, and the solution is made up to 1 litre.

The author finds that by means of Willstätter and Schüchli's method, 0.1—0.5 mg. of sugar can be estimated. However, this method cannot be employed in the estimation of sugar in blood. Blood containing 0.107% of sugar showed a content of 0.22% and 0.23% by this method. S. S. Z.

**Adsorption Compounds and Adsorption. V. The Adsorption Compounds of Cuprous Oxide.** L. BERCZELLER (*Biochem. Zeitsch.*, 1919, **93**, 230—237).—In precipitating cupric hydroxide from cupric salts with sodium hydroxide, some of the alkali is adsorbed by the cupric hydroxide. The black hydroxides adsorb more of it than the blue ones. Iodate ions are also adsorbed by cupric hydroxide, but in this case the blue hydroxides adsorb more of it than the black. The presence of sugar prevents the adsorption of sodium hydroxide by cupric hydroxide. S. S. Z.

**Estimation of Small Quantities of Sugar in the Presence of the Higher or Lower Products of Protein Degradation.** ERWIN LAST (*Biochem. Zeitsch.*, 1919, **93**, 66—82).—The higher products of protein degradation, such as albumoses and peptones, the presence of which interferes with the estimation of sugar, can be removed by means of mercuric chloride in neutral solution. The sugar can then be estimated by Bertrand's method. In the presence of acids, the precipitation of these products is incomplete. An excess of mercuric chloride must also be avoided in order to ensure good results. Two grams of mercuric chloride per gram of peptone are found to be a suitable quantity. The presence of monoaminoacids does not affect the accuracy of the sugar estimation by Bertrand's method; ereptone, however, does influence the results. This is due to the special atomic grouping in ereptone, which, on boiling with alkali hydroxide, liberates ammonia, and this dissolves some of the cuprous oxide. Ereptone can be removed from sugar solutions also by precipitation with mercuric chloride in neutral solution. The removal of both the higher and lower products of protein degradation with mercuric nitrate according to the Patein-Dufau method conduces to accurate results. S. S. Z.

**Estimation of Lactose in Altered Milks.** E. HELDT (*Bull. Soc. chim.*, 1919, [iv], **25**, 617—621).—A more detailed account of work already published (compare A., 1919, ii, 84).

W. G.



**Modification of the Phenylhydrazine Method for Estimating Pentosans.** PAUL MENAUL and C. T. DOWELL (*J. Ind. Eng. Chem.*, 1919, 11, 1024—1025).—The material is distilled with sulphuric acid instead of hydrochloric acid, and the furfuraldehyde is estimated in the distillate by precipitating with a known excess of phenylhydrazine, filtering off the hydrazone, and determining the excess of phenylhydrazine in the filtrate. For this purpose, an aliquot part of the filtrate is heated with ammoniacal copper sulphate solution, and the nitrogen evolved is measured, the reaction previously employed by Ebler for the determination of hydrazine (A., 1906, ii, 53) being quantitative also in the case of phenylhydrazine. [See, further, *J. Soc. Chem. Ind.*, 1920, 170A.]  
J. H. L.

**A Microchemical Method for the Estimation of Acetone.** M. RICHTER-QUITNER (*Biochem. Zeitsch.*, 1919, 93, 163—172).—A microchemical method in which 1—2 c.c. of urine and 1·5—3 c.c. of alkali need only be used. The urine is distilled once with steam in the presence of acetic acid, and a second time with dilute sulphuric acid. Blood or plasma need only be distilled once, and instead of the steam, air is passed through the heated flask. The titration of the distilled acetone is carried out with *N*/100-iodine and *N*/100-sodium thiosulphate. 0·1 Mg. of acetone in 100 c.c. can be estimated with accuracy by this method. The quantity of urine and blood used must contain not less than 0·04 mg. of acetone.  
S. S. Z.

**Microchemical Reactions of Veronal, Luminal, and Propional.** L. VAN ITALLE and A. L. W. E. VAN DER VEEN (*Pharm. Weekblad*, 1919, 56, 1112—1117; *J. Pharm. Chim.*, 1919, [vii], 20, 337—343).—Small traces of the derivatives of barbituric acid separated from urine by treatment with lead acetate and hydrogen sulphide may be converted into an easily identifiable, crystalline form by sublimation. Veronal may be separated as monoclinic crystals from its solution in sodium hydroxide by the addition of an acid, potassium dichromate, or ammonium phosphate. Lead acetate gives an amorphous mass, which becomes crystalline on boiling. Ammoniacal silver nitrate gives an irregular, crystalline mass of large, simple crystals of veronal-silver. With thallium nitrate, crystals of veronal-thallium are formed. Luminal and propional have only to be separated in the uncombined state. A crystal of ammonium phosphate introduced into a drop of a solution of these in sodium hydroxide causes the separation of the free acids in the form of drops which only gradually change into crystals, probably rhombic.  
W. J. W.

**Estimation of "Saccharin" in Urine.** GEORGE S. JAMIESON (*J. Biol. Chem.*, 1920, 41, 3—8).—Urine is treated with lead acetate and filtered. After acidifying with hydrochloric acid, the "saccharin" is extracted by ether, the ether removed by evapor-

ation, and the "saccharin" extracted from the residue by ether. The ether is removed, and the resulting residue is fused with sodium carbonate. From an estimation of sulphur in the fused product, the amount of "saccharin" may be deduced. J. C. D.

**The Estimation of Aniline in Commercial Anilines.**

WILLIAM JAMES SANDERSON and WILLIAM JACOB JONES (*J. Soc. Chem. Ind.*, 1920, **39**, 87).—A method of estimation is given which is based on a determination of the freezing point of the sample. The purity is deduced by reference to a table, which is provided, showing the freezing points of dry mixtures of aniline with varying proportions (1–7% by weight of the mixture) of each of benzene, phenylhydroxylamine, nitrosobenzene, *p*-aminophenol, nitrobenzene, *o*- or *p*-toluidine, *m*-phenylenediamine, and xylydine. J. K.

**Formaldehyde Titration of Amino-acids in Aqueous solutions or in Urine.**

W. MESTREZAT (*Bull. Soc. Chim. Biol.*, 1919, **1**, 107–113).—The methods employed by Ronchèse (cited by Maillard, *Compt. rend. Soc. Biol.*, 1911, **61**, 653) are insufficiently accurate. J. C. D.

**Urea and Hypobromite.**

L. LESCEUR (*J. Pharm. Chim.*, 1919, **20**, 305–314, 343–351, 374–381).—The volume of nitrogen liberated by the action of alkaline hypobromite solution on urea is always less than that required by theory; too low results are also found if the urea is calculated from the amount of carbon dioxide formed or of the hypobromite used in the reaction. The deficit is to some extent dependent on the proportion of free alkali present, and decreases, but never quite disappears, as the quantity of free alkali is increased; it appears to be due to the conversion of a part of the urea into sodium cyanate. W. P. S.

**Ureometer.**

P. SEYOR (*Ann. Chim. anal.*, 1920, [ii], **2**, 11–13).—The apparatus consists of a graduated tube open at its lower end, whilst the upper end, above the zero point, is bent over and downwards for a short distance, where it is blown out to form a bulb. A short side-tube with a tap is provided at the top of the bend. The bulb has a tubulure at the side into which is ground the neck of a small cylindrical bulb. The latter contains the hypobromite solution, whilst the urine or other liquid under examination is placed in the larger bulb. The whole apparatus is placed in a cylinder of water, the level of the latter then adjusted to the zero point by manipulating the tap, and the smaller bulb then turned (by means of the ground-in joint) so that the hypobromite solution mixes with the urine in the larger bulb. The evolved nitrogen displaces water from the graduated tube, and the volume of the nitrogen is noted after the water-level has been adjusted. If 1.3 c.c. of urine is taken for the estimation, each c.c. of nitrogen is equivalent to 1 gram of urea per litre of urine. W. P. S.

**Identification of Traces of Hydrocyanic Acid.** L. CHELLE (Bull. Soc. Pharm., Bordeaux, 1919; from Ann. Chim. anal., 1920, [ii], 2, 21—24. Compare A., 1919, ii, 529).—The following tests may be used for the identification of traces of hydrocyanic acid: *Phthalein test*.—A red coloration is obtained when a cyanide solution is treated with a drop of alkaline phenolphthalein solution reduced previously with zinc, and a drop of 0.1% copper sulphate is added. *isoPurpurate test*.—If a cyanide solution is heated with the addition of alkaline picric acid solution, an orange coloration develops after a few hours. *Ammoniacal silver iodide test*.—The reagent is prepared by diluting a mixture of 10 c.c. of *N*/1000. silver nitrate solution, 2 c.c. of ammonia, and five drops of 19% potassium iodide solution to 100 c.c.; this reagent gives a turbidity with a cyanide solution. For instance, if a turbidity is obtained when 1 c.c. of the cyanide solution is treated with 0.2 c.c. of the reagent, less than 0.001 mg. of hydrocyanic acid is present; with 0.005 mg. of hydrocyanic acid, 1 c.c. of the reagent is required. *Ferrocyanide test*.—This is the most characteristic reaction of hydrocyanic acid; it may be used for the identification of hydrocyanic acid in silver cyanide and mercuric cyanide. W. P. S.

**Sensitiveness of some Cyanide Reactions.** JOHN B. EKELEY and IGIE C. MACY (Proc. Colorado Sci. Soc., 1919, 11, 269—274).—Working directly with solutions of potassium cyanide, the Prussian blue test gives positive results (a blue precipitate on keeping) at a dilution of  $1:7 \times 10^4$  (at about  $1:17 \times 10^4$  for hydrogen cyanide). One hundred c.c. of potassium cyanide solution ( $1:7 \times 10^5$ ) give a definite result after acidifying with 10 c.c. of 1% tartaric acid and distilling off about 2 c.c.; this corresponds with a dilution of hydrogen cyanide about  $1:1.7 \times 10^6$ . The hanging-drop method with silver nitrate gives positive results with solutions of potassium cyanide ( $1:8 \times 10^6$ , corresponding with hydrogen cyanide at a dilution of about  $1:1.9 \times 10^6$ ) when 100 c.c. are exposed to the drop of silver nitrate for fifteen minutes. The Schönbein test gives positive results with potassium cyanide solutions at a dilution of  $1:1.8 \times 10^6$  in the light and  $1:2.3 \times 10^6$  in the dark (equivalent to  $1:4.3 \times 10^6$  and  $1:5.5 \times 10^6$ , respectively, for hydrogen cyanide). This test should be performed in closed vessels in the dark to secure trustworthy results, and only at extreme dilutions does it indicate the presence of hydrogen cyanide and exclude the presence of other substances (chlorine, bromine, hydrogen peroxide, hydrogen chloride) which are known to respond at high concentrations. CHEMICAL ABSTRACTS.

**Estimation and Separation of Pyridine and Ammonia.** E. B. R. PRIDEAUX (Trans. Faraday Soc., 1919, 15, 137—147).—Precise information as to the conditions for the titration of pyridine and of ammonia in the presence of pyridine, and of the separation of the two by distillation, has been obtained by application of the electrochemical theory. Congo-red is the correct

indicator for pyridine, and nitric acid the best acid. A correct indicator for the titration of ammonia in the presence of pyridine is  $\alpha$ -naphtholphthalein. Both ammonia and pyridine are estimated with sufficient accuracy provided that pyridine is not present in excess. Rosolic acid may be used if the bases are titrated directly, and the pyridine is present in amount considerably less than the ammonia. Ammonia and pyridine may be partly separated by distillation from a solution of which the acidity is maintained at about  $p_H=3$  to 4 (reddish-brown to Congo, orange to methyl-orange). The first part of the distillate contains most of the pyridine, the second most of the ammonia, so that the titrations just described may be used.

J. R. P.

**Estimation of Indole in Biological Media.** HARPER F. ZOLLER (*J. Biol. Chem.*, 1920, **41**, 25—36).—The usual preliminary steam distillation of the indole solution is abandoned and replaced by direct distillation, care being taken to have the solution adjusted to a hydrogen-ion concentration of  $p_H$  9.2 (see this vol., i, 250). The distillation is continued until all but about 10 c.c. have been driven over, the distillate being collected in a 100 c.c. volumetric flask and made up to the mark. A portion of the distillate containing not more than 0.20 mg. of indole is measured into a test-tube of convenient size, and two drops of 1.0% solution of sodium nitrite and five drops of concentrated sulphuric acid are added. The tube is shaken and left for five minutes for the nitroso-reaction to approach equilibrium. The contents are then extracted with three portions of 3 c.c. of *isobutyl* or *isoamyl* alcohol, each portion being drawn off with a pipette and placed in a test-tube having a 10 c.c. graduation. *isobutyl* or *isoamyl* alcohol is then added to bring the contents of the tube up to 10 c.c., and the colour is matched against a series of standards prepared by similar treatment of solutions containing a known amount of pure indole.

The method is stated to be simple, trustworthy, and rapid. The relative sensitivities of Herter's naphthaquinone reaction and the nitroso-reaction were found to be 1:2,000,000 and 1:1,500,000 respectively.

A warning is sounded against the use of the vanillin test proposed by Steensma (*A.*, 1906, ii, 315).

The rate at which the equilibrium of the nitroso-indole reaction is reached depends on the factors of concentration and temperature. At temperatures from 30—90°, the full depth of colour is obtained in a few seconds, but higher temperatures tend to destroy the coloured compound when in aqueous solutions. In pure *isobutyl* alcohol the colour is not destroyed by heating for several hours at 100°. In actual analyses, the test should not be carried out at temperatures above 30°.

J. C. D.

**Detection of other Cinchona Alkaloids in Salts of Quinine.**

I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 451—459).—Kerner and Weller's method has many disadvantages, and only gives

accurate results under certain conditions. The following method is suitable for quinine sulphate, but is inapplicable to other salts. 0.5 Gram of quinine sulphate is boiled gently for one minute with 250 mg. of sodium sulphate and 10 c.c. of water. Water is then added to restore the original volume, and the mixture cooled to 15°, with shaking. The liquid, with the precipitate, is kept below 18° for twenty-four hours, and then filtered through glass wool. Three drops of 4*N*-sodium hydroxide are added to the filtrate, which is then heated on the water-bath for half an hour. After twelve hours the solution is examined for the presence of a precipitate. The test is sensitive to 1% of cinchonidine. In regard to the nitroprusside test, the author does not confirm Krüss's opinion of its sensitiveness, and failed to devise a means of increasing this. De Vrij's chromate test is considered to be a suitable substitute for Kerner and Weller's method. For quinine bisulphate, 0.5 gram is boiled with 20 c.c. 2*N*-sodium acetate until the liquid is clear. Then 3 c.c. of 10% potassium chromate are added, and further treatment is carried out by de Vrij's method. For quinine, 0.5 gram is taken, together with 3 c.c. of *N*-sulphuric acid and 20 c.c. of 2*N*-sodium acetate, and the test continued as above. Quinine hydrochloride may be tested exactly as described by de Vrij.

W. J. W.

**Estimation of Albumin in Urine.** OTTO MAYER (*Zeitsch. anal. Chem.*, 1919, **58**, 337—346).—A reagent described previously by the author (*A.*, 1914, ii, 80) for the estimation of albumin in urine is altered in composition in order to render it more sensitive. Ten grams of mercuric chloride, 65 grams of sodium chloride, and 25 grams of citric acid are dissolved in 500 c.c. of hot water and the solution is filtered after a few days. This solution will give a ring reaction in about ten minutes with as little as 0.0002% of albumin whilst 0.001% of albumin is denoted by the appearance of a turbid zone within three minutes. If the urine contains more than 0.001% of albumin, the test is repeated after dilution until the reaction is just observable, and the quantity of albumin present then calculated from the degree of dilution.

W. P. S.

**Estimation of Catalase in Blood.** MEYER BODANSKY (*J. Biol. Chem.*, 1919, **40**, 127—130).—In making estimations of catalase by the method employed by Burge (*Amer. J. Physiol.*, 1916, **41**, 153), it was found that different samples of hydrogen peroxide often gave results which differed by 15–35%. It was experimentally shown that the reaction of the medium is one important factor in determining the activity of catalase. Consequently, caution must be exercised in maintaining uniform conditions when a series of determinations are being made.

J. C. D.











